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STOPPING WATER POLLUTION AT ITS SOURCE

MISA

Municipal/Industrial Strategy for Abatement

The Effluent Monitoring Regulation for the Petroleum Refining Sector

(Draft)

July 1987

Ontario
Ministry
of the
Environment

The Honourable
Jim Bradley
Minister

Rod McLeod
Deputy Minister

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The effluent monitoring
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THE EFFLUENT MONITORING REGULATION FOR THE PETROLEUM REFINING SECTOR
(DRAFT)

including

- **EXPLANATORY NOTES**
- **MISA ADVISORY COMMITTEE REPORT ON THE DRAFT REGULATION**
- **RESPONSES TO THE MISA ADVISORY COMMITTEE RECOMMENDATIONS ON THE DRAFT REGULATION**

JULY 1987

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FOREWORD

This document provides a draft of a Regulation made under Ontario's Environmental Protection Act. The draft Regulation is organized into sections grouped under the headings - Definitions, Application, Characterization, Routine Monitoring, Toxicity Testing, Flow Measurement, Sampling Requirements, Analytical Requirements and Reporting. Schedules are attached to the Regulation identifying Sampling Frequencies, Sampling Principles and Analytical Principles.

The Explanatory Notes are organized to parallel the Regulation headings in order to provide additional supporting information, and interpretation, to the legal text. Two supporting Appendices to the Explanatory Notes are provided. Appendix A provides information relating Ontario's Effluent Monitoring Priority Pollutant List to the chemical parameters in the Regulation. Appendix B describes flow measurement methods and devices.

A section consisting of the MISA Advisory Committee Report on the Effluent Monitoring Regulation for the Petroleum Refining Sector is included. This report makes recommendations regarding the draft regulation.

Finally, a section is provided with the summary of recommendations from the MISA Advisory Committee on the Draft Regulation, and the responses by the Ministry and/or the sectoral Joint Technical Committee. This is provided as additional explanation of the Regulation and actions the Ministry is taking to address issues raised by the MISA Advisory Committee.

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SECTION I

Draft Regulation Made Under

The Environmental Protection Act

Petroleum Refinery Effluent

DRAFT REGULATION MADE UNDER THE ENVIRONMENTAL PROTECTION ACT

PETROLEUM REFINERY EFFLUENT

DEFINITIONS

1.-(1) In this Regulation,

"analytical run" means a group of samples processed together through each step in an analytical process;

"composite sample" means a sample made up of three or more sub-samples which have been combined either automatically or manually;

"cooling water" means water that is used for the purpose of removing heat from process streams and that is not intended to come into contact with those process streams;

"cooling water sampling point" means a location on a cooling water stream prior to final discharge to a surface watercourse and before any discharge to a process effluent stream at a point after the process effluent sampling point;

"effluent" means any material discharged to a surface watercourse and includes process effluent, cooling water and storm water;

"effluent discharger" means a person responsible for a discharge of effluent to a surface watercourse;

"emergency overflow" means a diversion of storm water or a mixture of storm water and process effluent resulting from a change in normal hydraulic flow which by-passes its normal sampling point and ultimately discharges to a surface watercourse;

"emergency overflow sampling point" means a location on an emergency overflow stream prior to discharge to a surface watercourse and prior to dilution with once-through cooling water;

"grab sample" means an individual sample of at least 100 millilitres collected over a period not exceeding 15 minutes;

"landfarm leachate" means liquid collected from a sludge landfarm pursuant to a certificate of approval issued under section 38 of the Act;

"method blank sample" means an uncontaminated quality control sample processed through an entire analytical procedure;

"method detection limit" means the minimum measured concentration of a parameter which will imply with 95% confidence that the level of the parameter in the sample differs from zero, based on the cumulative variability introduced at every step in the analytical method;

"once through cooling water" means cooling water that has been circulated once through heat exchangers;

"primary flow measuring device" means a hydraulic structure which produces at a specified sensing location or set of locations a defined range of measurements which are uniquely related to the flowrate at that location or locations;

"process effluent" means waste water from petroleum refinery operations and includes water produced or used in processing, ballast water and wastes from water treatment facilities;

"process effluent sampling point" means a location in a process effluent stream following final treatment but prior to dilution with once-through cooling water;

"quality assurance" means the assurance that data of proven and known quality is being provided by effluent dischargers through a system of quality control activities and documentation;

"quality control" means the operations undertaken by an effluent discharger to ensure that data produced are generated within known probability limits of accuracy and precision;

"reagent blank sample" means a quality control sample of reagents used in an analytical run but excluding any sample of effluent;

"replicate sample" means one of at least two aliquots removed from a single sample container for a given analytical test group;

"sample" means a composite sample or one or more grab samples of effluent taken pursuant to section 13;

"secondary flow measuring device" means a device or combination of devices which converts information from sensors on a primary flow measuring device into flowrate data according to the characteristic of the primary flow measuring device;

"set of samples" means the number of samples that an effluent discharger must collect at a sampling point in order to perform all of the analyses required by this Regulation;

"significant process change" means any change in equipment or in a production or treatment process which may adversely affect the quality of process effluent;

"spiked method blank sample" means a quality control sample of uncontaminated water to which a known amount of standard solution is added;

"spiked sample" means a quality control sample to which a known amount of a standard solution is added;

"standard reference material" means an analytical reagent of a certified purity obtained from the United States National Bureau of Standards or the United States Environmental Protection Agency, or an equivalent agency;

"standard solution" means a solution of a chemical or group of chemicals, the concentration of which is validated using a standard reference material, where an appropriate standard reference material is available;

"static 96 hour LC50 toxicity test" means a test which uses graded concentrations of effluent to establish the concentration of effluent that is lethal to fifty per cent of rainbow trout fingerlings over a 96-hour period;

"storm water" means contaminated or potentially contaminated water run-off that results from precipitation of any kind that falls on a works;

"storm water sampling point" means a location on a storm water stream prior to final discharge to a surface watercourse;

"surface watercourse" means any lake, river, swamp, stream or drainage works;

"three month period" means a period of time beginning on January 1st, April 1st, July 1st or October 1st of each year;

"travelling blank sample" means a quality control sample of uncontaminated water which has been opened and resealed at a sampling point and which accompanies a set of samples from the sampling point to the laboratory for analysis;

"travelling spiked blank sample" means a quality control sample of uncontaminated water to which an amount of standard solution is added in the laboratory a maximum of 24 hours prior to accompanying a set of sample containers from the laboratory to the sampling point and back to the laboratory for analysis with the set of samples;

"works" means a refinery referred to in subsection 2(1) and the associated property under common ownership, control or management;

"variable flowrate" means a flowrate within a day which exceeds plus or minus 15% of the daily mean flow more than 10% of the days of the year.

(2) The purpose of this Regulation is to establish a data base on effluent quality in the petroleum refinery class which will be applied to the development of effluent limits.

APPLICATION

2.-(1) The following refineries are classified as effluent dischargers in the petroleum refinery class:

1. Esso Petroleum Canada, a division of Imperial Oil Limited, (Sarnia Refinery)
2. Petro-Canada Inc. (Clarkson Refinery)
3. Petro-Canada Inc. (Trafalgar Refinery)
4. Petrosar Limited (Corunna Manufacturing Complex)
5. Shell Canada Limited (Sarnia Manufacturing Centre)
6. Suncor Inc., Sunoco Division (Sarnia Refinery)
7. Texaco Canada Inc. (Nanticoke Refinery)

(2) This regulation applies to each effluent discharger in the petroleum refinery class.

3.-(1) Sections 4 through 12 of this Regulation come into force 6 months after the date of filing.

(2) Sections 6 through 11 of this Regulation cease to apply 18 months after the date of filing.

CHARACTERIZATION

4. Each effluent discharger shall collect a set of samples from each process effluent sampling point of that discharger,

(a) once within 3 months of the date of the collection of the first samples pursuant to section 5,

(b) once at least 6 months following but not later than 9 months from the date of the collection of samples pursuant to clause (a),

(c) once in 1991 and in every third calendar year thereafter, and

(d) once within 30 days of every significant process change,

and analyze for the parameters in Column 2 of Schedule 1.

ROUTINE MONITORING

5.-(1) Except as provided in subsection (2), each effluent discharger shall collect one set of samples during each operating day from each process effluent sampling point of that discharger and analyze for the parameters in Column 2 of Schedule 1 which are marked with an "x" in Column 4 of Schedule 1.

(2) Subsection (1) does not apply to days on which samples cannot be collected or analyzed because of equipment malfunction or failure, except to those days in excess of 3 in number in any one month.

6.-(1) On at least three separate operating days in each week, each effluent discharger shall collect one set of samples from each process effluent sampling point of that discharger and analyze for,

(a) the parameters in Column 2 of Schedule 1 which are marked with an "x" in Column 5 of Schedule 1; and

(b) where chromium or zinc are used in the treatment of cooling water by that discharger, the parameters in Column 2 of Schedule 1 which are marked with a "y" in Column 5 of Schedule 1.

(2) Subsection (1) does not apply to days on which samples cannot be collected or analyzed because of equipment malfunction or failure, except to those days in excess of 1 in number in any one month.

7.-(1) On at least three separate operating days in one week in each three-month period, each effluent discharger shall collect one set of samples from each process effluent sampling point of that discharger and analyze for the parameters in Column 2 of Schedule 1 which are marked with an "x" in Column 6 of Schedule 1.

(2) For the purposes of subsection (1), subsequent sampling shall take place no less than six weeks and no more than four months from the previous sampling.

8. At least once in each month, each effluent discharger shall collect one set of samples from each cooling water sampling point of that discharger and analyze for the parameters in Column 2 of Schedule 1 which are marked with an "x" in Column 7 of Schedule 1.

9.-(1) Each effluent discharger shall collect one set of samples from each storm water sampling point during each discharge of storm water to a surface watercourse and analyze for the parameters in Column 2 of Schedule 1 which are marked with an "x" in Column 5 of Schedule 1.

(2) Each effluent discharger shall collect one set of samples from each emergency overflow sampling point during the first flush of the overflow and analyze for the parameters in Column 2 of Schedule 1 which are marked with an "x" in Column 5 of Schedule 1.

10.-(1) At least once in each year, each effluent discharger shall collect one set of samples from a discharge of landfarm leachate to a surface watercourse and analyze for the parameters in Column 2 of Schedule 1 which are marked with an "x" in Column 6 of Schedule 1.

(2) At least once during each discharge of landfarm leachate to a surface watercourse, each effluent discharger shall collect one set of samples from the discharge and analyze for the parameters in Column 2 of Schedule 1 which are marked with an "x" in Column 5 of Schedule 1.

TOXICITY TESTING

11. Each effluent discharger shall collect a sample,

(a) once in each calendar month from each process effluent sampling point, and

(b) once in each three-month period from each cooling water sampling point,

and perform a static 96 hour LC50 toxicity test according to the procedure described in the Ministry of the Environment publication entitled "Protocol to Determine the Acute Lethality of Liquid Effluents to Fish" dated July 1983.

FLOW MEASUREMENT

12.-(1) Each effluent discharger shall continuously measure and record the flowrate of each process effluent stream at a location or locations representative of the flowrate at the process effluent sampling point.

(2) Subsection (1) does not apply to days on which flowrate cannot be measured because of equipment malfunction or failure except to those days in excess of 3 in number in any one month.

(3) Methods and devices for continuous flow measurement shall be accurate to within plus or minus 5% of the actual flowrate for the primary flow measuring device and plus or minus 2% of fullscale flowrate for the secondary flow measuring device, for the design range of the flow measuring system.

(4) Each effluent discharger shall measure and record or calculate by water balance the flowrate at each cooling water sampling point at the time of each sampling.

(5) Each effluent discharger shall measure and record the volume and duration at each landfarm leachate sampling point for each discharge of landfarm leachate.

(6) Each effluent discharger shall measure and record the flowrate at each storm water sampling point at the time of each sampling.

(7) Methods and devices or calculations for the measurement of flow at the time of sampling shall be accurate to within plus or minus 20% of the actual flowrate.

(8) Prior to the taking of any samples required pursuant to section 5, each effluent discharger shall,

(a) ensure that all flow measuring devices have been installed in a manner to ensure accurate performance; and

(b) ensure that all secondary flow measuring devices have been field calibrated to ensure accurate performance.

(9) All flow measuring devices shall be maintained according to good operating practices and the recommendations of the manufacturer or designer.

(10) The calibration of all secondary flow measuring devices shall be verified at regular intervals not exceeding one year by a competent person according to the recommendations of the manufacturer or designer.

(11) Records of maintenance and calibration verification shall be maintained by each effluent discharger.

SAMPLING REQUIREMENTS

13.-(1) Each sample must be taken at an appropriate location and point in the effluent stream to ensure that the sample is representative of the effluent at the sampling point, having regard to the characteristics of each parameter to be analyzed for in the sample, using the appropriate sample container, container pretreatment and sampling precautions specified for the sample in Columns 2, 3 and 4 of Schedule 2.

(2) Each sample collected from a process effluent sampling point shall be taken in the following manner:

1. At sampling points which have a variable flowrate, samples for parameters in all analytical test groups in Schedule 1, except those numbered 15, 16, 17, 18 and 25, shall be taken over a 24-hour period,

   (i) using a composite sampling device which operates continuously and automatically adjusts the volume of sub-sample collected or the time interval between sub-samples to the rate of flow in the effluent stream; or

   (ii) a minimum of eight times evenly spaced over the 24-hour period and combined in proportion to flow.

2. At sampling points which do not have a variable flowrate, composite samples for parameters in all analytical test groups in Schedule 1, except those numbered 15, 16, 17, 18 and 25, shall be taken as specified in paragraph 1 or by combining at the sampling point equal volume sub-samples which have been taken over a 24-hour period and which,

   (i) if taken by an automatic sampling device, have been taken at intervals not exceeding 15 minutes, or

(ii) if taken manually, have been taken a minimum of 8 times evenly spaced over the 24-hour period and combined in equal volumes.

3. For samples taken for parameters in the analytical test groups numbered 15, 16, 17, 18 and 25 in Schedule 1, three equal volume grab samples shall be taken at intervals of at least 6 hours over a 24-hour period and combined.

(3) Each sample collected from a cooling water sampling point shall consist of three equal volume grab samples taken at intervals of at least 6 hours over a 24-hour period and combined or alternatively pursuant to the provisions of subsection (2).

(4) Each sample collected from a storm water sampling point, an emergency overflow sampling point or a landfarm leachate discharge shall consist of one grab sample.

(5) Composite samples which are to be analyzed for parameters in the analytical test groups numbered 2 and 14 in Schedule 1 shall be collected in separate containers, to which the preservatives specified for those parameters in Column 6 of Schedule 2 have been added prior to sampling.

(6) Each multi-parameter composite sample shall be continuously stirred while being sub-aliquotted into the appropriate container for the parameters set out in Column 2 of Schedule 2.

(7) Grab samples for parameters in the analytical test groups numbered 16, 17 and 18 in Schedule 1 shall be combined in the purge vessel in the laboratory.

(8) Grab samples for the parameters in the analytical test group numbered 25 in Schedule 1, shall be combined in total, including solvent rinsings of the containers, in the laboratory immediately prior to extraction.

(9) The volume of all samples submitted to the laboratory for analysis shall be at least the minimum sample volume specified in Column 5 of Schedule 2 for each parameter.

(10) All samples, including sub-samples, composite samples and grab samples, shall be cooled immediately to between 4°C and 10°C and stored at that temperature until analysed.

(11) All samples shall be preserved immediately according to the appropriate preservation method specified for each parameter in Column 6 of Schedule 2.

(12) Samples must be properly and completely labelled or coded to indicate sampling point, time, date, sample type, identification of effluent discharger and analysis to be performed.

(13) Samples must be transported as soon as practicable to a laboratory for analysis.

(14) Each sample shall be analyzed within the times specified in Column 7 of Schedule 2.

(15) Records of all samples taken, containing the date and time of sampling, the flow rate, sampling procedure and all other relevant details shall be maintained by each effluent discharger.

(16) Each effluent discharger shall ensure that only qualified personnel are engaged in sampling operations and in the maintenance of sampling equipment used.

(17) Each effluent discharger shall develop a maintenance schedule for all sampling equipment and keep records of all maintenance performed.

(18) Each effluent discharger shall ensure that all sample containers are clean and free of the analytes of interest at the time of sampling.

(19) Each effluent discharger shall collect the quality control samples set out in subsection (21) from one process effluent sampling point once per month concurrent with sampling required pursuant to section 6 and analyze for the parameters in Column 2 of Schedule 1 which are marked with an "x" in Column 5 of Schedule 1.

(20) Each effluent discharger shall collect the quality control samples set out in subsection (21) from one process effluent sampling point once in each three-month period concurrent with sampling required pursuant to section 7 and analyze for the parameters in Column 2 of Schedule 1 which are marked with an "x" in Column 6 and which are not marked with an "x" in Column 5 of Schedule 1.

(21) For the purposes of subsections (19) and (20), quality control sample means,

(a) For each sample collected for parameters in all analytical test groups in Schedule 1, one duplicate sample;

(b) For each sample collected for parameters in each analytical test group in Schedule 1 except those groups numbered 1, 3 and 8, one travelling blank sample; and

(c) For each sample collected for parameters in the analytical test groups numbered 16 to 24, 26 and 27 in Schedule 1, one travelling spiked blank sample.

ANALYTICAL REQUIREMENTS

14.-(1) All analytical methods must meet generally accepted principles of good laboratory practice, including quality control activities, be appropriate to the type of sample to be analyzed, quantitatively recover target parameters from effluent samples, identify the target parameters and accurately quantify their concentration at and above the relevant method detection limits.

(2) All analytical procedures must be carried out by properly trained and qualified laboratory personnel in a properly equipped and maintained laboratory environment.

(3) All samples collected pursuant to Section 4 must be analyzed using procedures based on the applicable sample preparation and instrumental measurement method principles specified for each parameter in Columns 3 and 4 of Schedule 3 and using a method detection limit calculated for each parameter following the "Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11" adopted by the United States Environmental Protection Agency in 40 CFR 136, Appendix B but not exceeding the maximum method detection limit specified for each parameter in Column 6 of Schedule 3.

(4) All samples collected pursuant to Sections 5, 6, 7, 8, 9, 10 and 13 and subsections (6) and (7) must be analyzed using,

(a) the applicable sample preparation method principles set out for each parameter in Column 3 of Schedule 3;

(b) the applicable instrumental measurement method principles set out in Column 4 of Schedule 3 or alternate instrumental measurement method principles set out in Column 5 of Schedule 3; and

(c) a method detection limit calculated for each parameter following the "Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11" adopted by the United

States Environmental Protection Agency in 40 CFR 136, Appendix B but not exceeding the maximum method detection limit specified for each parameter in Column 6 of Schedule 3.

(5) All analytical measurement systems must be regularly calibrated in the following manner:

1. Calibration standards shall be validated using standard reference material, where available.

2. A calibration curve of concentration or weight versus instrument response shall be established within the response range normally encountered in typical samples.

3. Except for the analytical test groups numbered 3 and 7 in Schedule 1, samples may be diluted or concentrated to permit measurement within the concentration range established by the calibration curve.

4. Control limits shall be established within which a daily calibration curve must fall.

5. Before calculating results of all samples from an analytical run, the reagent blank sample shall be shown to fall within control limits and the analytical measurement adjusted accordingly.

(6) Concurrent with the analysis of every twelve samples collected pursuant to sections 4 through 10 which are analyzed for a parameter in any analytical test group, except those numbered 3, 8, 11 and 25 in Schedule 1, at least one of each of the following laboratory performance samples shall be analyzed:

1. a randomly selected replicate sample or, where sample volume is insufficient, a randomly selected duplicate sample,

2. a method blank sample,

3. a spiked method blank sample, and

4. a spiked sample.

(7) Concurrent with the analysis of every six samples collected pursuant to sections 4 through 10 which are analyzed for a parameter in those analytical test groups numbered 3, 8, 11 and 25 in Schedule 1, at least one of each of the following laboratory performance samples shall be analyzed:

1. a randomly selected replicate sample or, where sample volume is insufficient, a randomly selected duplicate sample, and
2. a method blank sample,

(8) Records for the operations referred to in subsections (5), (6) and (7) above shall be maintained at the laboratory.

REPORTING

15.-(1) Within 3 months of the date this Regulation comes into force, each effluent discharger shall provide the following information in a report acceptable to the Director:

1. A plot plan showing the location of all processing areas, intakes, process effluent streams, cooling water streams, storm water streams, emergency overflows, outfalls, sampling points and flow measuring devices.
2. A description of the types and quantities of chemicals added to once-through cooling water.
3. A description of sampling methods and devices employed.
4. A description of flow measurement methods and devices employed and a calibration report as proof of accuracy of those devices.
5. The name and address of the laboratory or laboratories which will carry out the analytical work.
6. A description of the analytical procedures used in the laboratory, including quality control and quality assurance procedures.
7. A schedule of sampling dates and times by location.
8. A schedule of reporting analytical results to the Director for analysis to be performed by outside laboratories pursuant to this Regulation.

(2) Each effluent discharger shall report any changes to the information submitted pursuant to subsection (1) to the Director within thirty days of any change.

(3) The results of all analyses performed by or on behalf of an effluent discharger on samples collected in each month pursuant to Sections 4 through 11 and 13, which have been certified as authentic by an official of the effluent discharger who has been duly authorized by the effluent discharger for such purpose, shall be reported to the Director in a written form and in an electronic format on floppy diskette, by the end of the month following the month in which the sampling was conducted.

(4) The following information, which has been certified as authentic by an official of the effluent discharger who has been duly authorized by the effluent discharger for such purpose, shall be reported to the Director on a monthly basis in a written form and in an electronic format on floppy diskette, by the end of the month following the date of measurement:

1. The daily maximum, minimum and mean flows from continuous flow measurement.
2. The flow at the time of sampling at each cooling water and storm water sampling point.
3. The approximate volume discharged and duration of each landfarm leachate discharge.
4. The location and approximate duration of each emergency overflow.
5. The approximate duration of each discharge of storm water to a surface watercourse.

(5) By the end of each month, each effluent discharger shall submit a report to the Director which summarizes the quantities of and the dates on which chemicals were added to once-through cooling water in the preceding month and the date, duration and cause of each malfunction or failure of sampling, analytical and flow measurement equipment.

COLUMN DESCRIPTIONS FOR SCHEDULE 1

Column 2:
- all parameters to be analysed in characterization samples

Column 3:
- CAS = Chemical Abstract Series Number

Column 4:
- daily for process effluents only

Column 5:
- 3 times per week for process effluents
- during discharge for stormwater, emergency overflows and landfarm leachate

Column 6:
- 3 daily samples within one week, each quarter for process effluent
- once per year for landfarm leachate

Column 7:
- once per month for cooling water

SCHEDULE 1 - MONITORING PARAMETERS AND FREQUENCIES

	COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6	COLUMN 7
ANALYTICAL TEST GROUP		CHARACTERIZATION PARAMETERS	CAS #'S				
#	NAME						
1	Chemical Oxygen Demand	Chemical oxygen demand (COD)	N/A			X	
2	Cyanide	Cyanide	57-12-5			X	
3	Hydrogen ion (pH)	Hydrogen ion (pH)	N/A	X	X	X	X
4a	Nitrogen	Ammonia plus Ammonium	N/A		X	X	
		Total Kjeldahl nitrogen	N/A			X	
4b		Nitrate	N/A			X	
		Nitrite	N/A			X	
5	Organic carbon	Dissolved organic carbon (DOC)	N/A			X	
		Total organic carbon (TOC)	N/A		X	X	X
6	Total phosphorus	Total phosphorus	N/A		X	X	X
7	Specific conductance	Specific conductance	N/A			X	
8	Suspended solids	Total suspended solids (TSS)	N/A		X	X	X
		Volatile suspended solids (VSS)	N/A	X	X	X	X

SCHEDULE 1 - MONITORING PARAMETERS AND FREQUENCIES

	COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6	COLUMN 7
ANALYTICAL TEST GROUP		CHARACTERIZATION PARAMETERS	CAS #'S				
#	NAME						
9	Total metals	Aluminum	7429-90-5			X	
		Beryllium	7440-41-7			X	
		Cadmium	7440-43-9			X	
		Chromium	7440-47-3		Y	X	
		Cobalt	7440-48-4			X	
		Copper	7440-50-8			X	
		Lead	7439-92-1			X	
		Molybdenum	7439-98-7			X	
		Nickel	7440-02-0			X	
		Silver	7440-22-4			X	
		Thallium	7440-28-0			X	
		Vanadium	7440-62-2			X	
		Zinc	7440-66-6		Y	X	
10	Hydrides	Antimony	7440-36-0			X	
		Arsenic	7440-38-2			X	
		Selenium	7782-49-2			X	
11	Chromium (Hexavalent)	Chromium (Hexavalent)	7440-47-3			X	
12	Mercury	Mercury	7439-97-6			X	
13	Total alkyl lead	Tetra-alkyl lead	N/A			X	
		Tri-alkyl lead	N/A			X	
14	Phenolics (4AAP)	Phenolics (4AAP)	N/A	X	X	X	X
15	Sulphide	Sulphide	N/A		X	X	X

SCHEDULE 1 - MONITORING PARAMETERS AND FREQUENCIES

	COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6	COLUMN 7
ANALYTICAL TEST GROUP		CHARACTERIZATION PARAMETERS	CAS #'S				
#	NAME						
16	Volatiles, Halogenated	1,1,2,2-Tetrachloroethane	79-34-5			X	
		1,1,2-Trichloroethane	79-00-5			X	
		1,1-Dichloroethane	75-34-3			X	
		1,1-Dichloroethylene	75-35-4			X	
		1,2-Dichlorobenzene	95-50-1			X	
		1,2-Dichloroethane (Ethylene dichloride)	107-06-2			X	
		1,2-Dichloropropane	78-87-5			X	
		1,3-Dichlorobenzene	541-73-1			X	
		1,4-Dichlorobenzene	106-46-7			X	
		Bromoform	75-25-2			X	
		Bromomethane	74-83-9			X	
		Carbon tetrachloride	56-23-5			X	
		Chlorobenzene	108-90-7			X	
		Chloroform	67-66-3			X	
		Chloromethane	74-87-3			X	
		Cis-1,3-Dichloropropylene	10061-01-5			X	
		Dibromochloromethane	124-48-1			X	
		Dichlorobromomethane	75-27-4			X	
		Ethylene dibromide	106-93-4			X	
		Methylene chloride	75-09-2			X	
		Tetrachloroethylene (Perchloroethylene)	127-18-4			X	
		Trans-1,2-Dichloroethylene	156-60-5			X	
		Trans-1,3-Dichloropropylene	10061-02-6			X	
		Trichloroethylene	79-01-6			X	
		Trichlorofluoromethane	75-69-4			X	
		Vinyl chloride (Chloroethylene)	75-01-4			X	

SCHEDULE 1 - MONITORING PARAMETERS AND FREQUENCIES

	COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6	COLUMN 7
ANALYTICAL TEST GROUP		CHARACTERIZATION PARAMETERS	CAS #'S				
#	NAME						
17	Volatiles, Non-Halogenated	Benzene	71-43-2		X	X	X
		Ethylbenzene	100-41-4		X	X	X
		Methyl ethyl ketone	78-93-3			X	
		Styrene	100-42-5			X	
		Toluene	108-88-3		X	X	X
		o-Xylene	95-47-6		X	X	X
		m-Xylene and p-Xylene (NOTE 1)	N/A		X	X	X
18	Volatiles, Water Soluble	Acrolein	107-02-8				
		Acrylonitrile	107-13-1				
		1,3-Butadiene	106-99-0				

SCHEDULE 1 - MONITORING PARAMETERS AND FREQUENCIES

	COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6	COLUMN 7
ANALYTICAL TEST GROUP		CHARACTERIZATION PARAMETERS	CAS #'S				
#	NAME						
19	Extractables, Base Neutral	Acenaphthene	83-32-9			X	
		5-nitro Acenaphthene	602-87-9			X	
		Acenaphthylene	208-96-8			X	
		Anthracene	120-12-7			X	
		Benz(a)anthracene	56-55-3			X	
		Benzo(a)pyrene	50-32-8			X	
		Benzo(b)fluoranthene	205-99-2			X	
		Benzo(ghi)perylene	191-24-2			X	
		Benzo(k)fluoranthene	207-08-9			X	
		Camphene	79-92-5			X	
		1-Chloronaphthalene	90-13-1			X	
		2-Chloronaphthalene	91-58-7			X	
		Chrysene	218-01-9			X	
		Dibenz(a,h)anthracene	53-70-3			X	
		Fluoranthene	206-44-0			X	
		Fluorene	86-73-7			X	
		Indeno(1,2,3-cd)pyrene	193-39-5			X	
		Indole	120-72-9			X	
		1-Methylnaphthalene	90-12-0			X	
		2-Methylnaphthalene	91-57-6			X	
		Naphthalene	91-20-3			X	
		Perylene	198-55-0			X	
		Phenanthrene	85-01-8			X	
		Pyrene	129-00-0			X	

SCHEDULE 1 - MONITORING PARAMETERS AND FREQUENCIES

	COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6	COLUMN 7
ANALYTICAL TEST GROUP		CHARACTERIZATION PARAMETERS	CAS #'S				
#	NAME						
19	Extractables, Base Neutral	Benzyl butyl phthalate	85-68-7				
	(continued)	Bis(2-ethyhexyl) phthalate	111-81-7				
		Di-n-butyl phthalate	84-74-2				
		Di-n-octyl phthalate	117-81-7				
		4-Bromophenyl phenyl ether	101-55-3				
		4-Chlorophenyl phenyl ether	7005-72-3				
		Bis(2-chloroisopropyl)ether	108-60-1				
		Bis(2-chloroethyl)ether	111-44-4				
		Diphenyl ether	101-84-8				
		2,4-Dinitrotoluene	121-14-2				
		2,6-Dinitrotoluene	606-20-2				
		Bis(2-chloroethoxy)methane	111-91-1				
		Diphenylamine	122-39-4				
		N-Nitrosodiphenylamine	86-30-6				
		N-Nitrosodi-n-propylamine	621-64-7				

SCHEDULE 1 - MONITORING PARAMETERS AND FREQUENCIES

COLUMN 1		COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6	COLUMN 7
ANALYTICAL TEST GROUP		CHARACTERIZATION PARAMETERS	CAS #'S				
#	NAME						
20	Extractables, Acid (Phenolics)	2,3,4,5-Tetrachlorophenol	4901-51-3			X	
		2,3,4,6-Tetrachlorophenol	58-90-2			X	
		2,3,5,6-Tetrachlorophenol	935-95-5			X	
		2,3,4-Trichlorophenol	15950-66-0			X	
		2,3,5-Trichlorophenol	933-78-8			X	
		2,4,5-Trichlorophenol	95-95-4			X	
		2,4,6-Trichlorophenol	88-06-2			X	
		2,4-Dimethyl phenol	105-67-9			X	
		2,4-Dinitrophenol	51-28-5			X	
		2,4-Dichlorophenol	120-83-2			X	
		2,6-Dichlorophenol	87-65-0			X	
		4,6-Dinitro-o-cresol	534-52-1			X	
		2-Chlorophenol	95-57-8			X	
		4-Chloro-3-methylphenol	59-50-7			X	
		4-Nitrophenol	100-02-7			X	
		m-Cresol	108-39-4			X	
		o-Cresol	95-48-7			X	
		p-Cresol	106-44-5			X	
		Pentachlorophenol	87-86-5			X	
		Phenol	108-95-2			X	
21	Extractables, Phenoxy Acid Herbicides		N/A				
22	Extractables, Organochlorine Pesticides		N/A				

SCHEDULE 2 - SAMPLING PRINCIPLES

Column 1	Column 2	Column 3	Column 4	Col. 5	Column 6	Column 7
ANALYTIC TEST GROUP #	SAMPLE CONTAINER	CONTAINER PRE-TREATMENT	TEST SPECIFIC SAMPLING PRECAUTIONS	MIN. SAM. VOL.	PRESERVATION METHOD*	STORAGE TIME
1	Polyethylene terephthalate (PET/PET-G) with unlined polypropylene lid, glass, polystyrene or polyethYlene with unlined polypropylene lid.	Generally no pretreatment required for new containers.	If sample is high (>5%) in hydrocarbons or organic solvents use glass sample container only.	25 mL	Add maximum of 10 mL/L of 50% sulphuric acid (containing <1 mg/L of all analytes) prior to sampling or add maximum of 5 mL/L of concentrated sulphuric acid immediately after sampling to lower pH to <2.	28 days
2	1L Boston round, clear glass with plastic lined screw cap.	If pre-treatment necessary, wash in hot detergent water solution followed by several rinses in distilled water.	None	500 mL	Add NaOH (cyanide free) to raise pH to 12.	7 days
3	Polyethylene terephthalate (PET/PET-G) with unlined polypropylene lid, glass, polystyrene or polyethylene with unlined polypropylene lid.	Generally no pretreatment required for new containers.	If sample is high (>5%) in hydrocarbons or organic solvents use glass sample container only.	50 mL	None	3 days
4a	Polyethylene terephthalate (PET/PET-G) with unlined polypropylene lid, glass, polystyrene or polyethylene with unlined polypropylene lid.	Generally no pretreatment required for new containers.	If sample is high (>5%) in hydrocarbons or organic solvents use glass sample container only.	100 mL	Add maximum of 10 mL/L of 50% sulphuric acid (containing <1 mg/L of all analytes) prior to sampling or add maximum of 5 mL/L of concentrated sulphuric acid immediately after sampling to lower pH to <2.	10 days

SCHEDULE 2 - SAMPLING PRINCIPLES

Column 1 ANALYTIC TEST GROUP #	Column 2 SAMPLE CONTAINER	Column 3 CONTAINER PRE-TREATMENT	Column 4 TEST SPECIFIC SAMPLING PRECAUTIONS	Col. 5 MIN. SAM. VOL.	Column 6 PRESERVATION METHOD*	Column 7 STORAGE TIME
4b	Polyethylene terephthalate (PET/PET-G) with unlined polypropylene lid, glass, polystyrene or polyethylene with unlined polypropylene lid.	Generally no pretreatment required for new containers.	If sample is high (>5%) in hydrocarbons or organic solvents use glass sample container only.	50 mL	None	2 days
5	Polyethylene terephthalate (PET/PET-G) with unlined polypropylene lid, glass, polystyrene or polyethylene with unlined polypropylene lid.	Generally no pretreatment required for new containers.	If sample is high (>5%) in hydrocarbons or organic solvents use glass sample container only.	100 mL	Add maximum of 10 mL/L of 50% sulphuric acid (containing <1 mg/L of all analytes) prior to sampling or add maximum of 5 mL/L of concentrated sulphuric acid immediately after sampling to lower pH to <2.	5 days
6	Polyethylene terephthalate (PET/PET-G) with unlined polypropylene lid, glass, polystyrene or polyethylene with unlined polypropylene lid.	Generally no pretreatment required for new containers.	If sample is high (>5%) in hydrocarbons or organic solvents use glass sample container only.	75 mL	Add maximum of 10 mL/L of 50% sulphuric acid (containing <1 mg/L of all analytes) prior to sampling or add maximum of 5 mL/L of concentrated sulphuric acid immediately after sampling to lower pH to <2.	28 days
7	Polyethylene terephthalate (PET/PET-G) with unlined polypropylene lid, glass, polystyrene or polyethylene with unlined polypropylene lid.	Generally no pretreatment required for new containers.	If sample is high (>5%) in hydrocarbons or organic solvents use glass sample container only.	75 mL	None	3 days

SCHEDULE 2 - SAMPLING PRINCIPLES

Column 1	Column 2	Column 3	Column 4	Col. 5	Column 6	Column 7
ANALYTIC TEST GROUP #	SAMPLE CONTAINER	CONTAINER PRE-TREATMENT	TEST SPECIFIC SAMPLING PRECAUTIONS	MIN. SAM. VOL.	PRESERVATION METHOD*	STORAGE TIME
8	Polyethylene terephthalate (PET/PET-G) with unlined polypropylene lid, glass with foil lined lid, polystyrene or polyethylene with unlined polypropylene lid.	Generally no pretreatment required for new containers.	If sample is high (>5%) in hydrocarbons or organic solvents use glass sample container only.	500 mL	None	7 days
9	Polyethylene terephthalate (PET/PET-G) with unlined polypropylene lid, polyethylene or polystyrene.	If pre-treatment necessary, soak overnight in a 5% solution of HNO3, followed by several rinses in distilled water.	None	900 mL	Add HNO3 (containing < 1mg/L of all analytes) to lower pH to less than 2.	30 days
10	Polyethylene terephthalate (PET/PET-G) with unlined polypropylene lid, polyethylene, polystyrene or 1L Boston round, clear glass with plastic lined screw cap.	If pre-treatment necessary, soak overnight in a 5% solution of HNO3, followed by several rinses in distilled water.	None	50 mL	Either none or as for metals, if to be analyzed from same sample.	30 days
11	Amber glass with teflon lined screw cap.	If pre-treatment necessary, soak overnight in a 5% solution of HNO3, followed by several rinses in distilled water.	None	100 mL	None	3 days

SCHEDULE 2 - SAMPLING PRINCIPLES

Column 1	Column 2	Column 3	Column 4	Col. 5	Column 6	Column 7
ANALYTIC TEST GROUP #	SAMPLE CONTAINER	CONTAINER PRE-TREATMENT	TEST SPECIFIC SAMPLING PRECAUTIONS	MIN. SAM. VOL.	PRESERVATION METHOD*	STORAGE TIME
12	1L Boston round, clear glass with plastic lined screw cap.	If pre-treatment necessary, soak overnight in a 5% solution of HNO3, followed by several rinses in distilled water.	No sample contact with metal.	200 mL	Add 1-2 mL HNO3 per 250 mL sample followed by at least .5 mL K2Cr2O7 solution to produce definite yellow colour.	7 days
13	Amber glass with teflon lined screw cap.	If pre-treatment necessary, soak overnight in a 5% solution of HNO3, followed by several rinses in distilled water.	Fill bottle to top-no air space.	4 L	None	4 days
14	Glass with non-phenolic cap/liner/glue.	Generally no pretreatment required for new containers.	None	250 mL	Add maximum of 10 mL/L of 50% sulphuric acid solution (containing <1 mg/L of all analytes) prior to sampling to lower pH to <2.	3 days
15	1L Boston round, clear glass with plastic lined screw cap.	If pre-treatment necessary, wash in hot detergent water solution, followed by several rinses in distilled water.	Cap sample container as soon as possible.	500 mL	Add 2 mL 2N Zinc Acetate solution followed dropwise by 5% Sodium Carbonate or 5% Sodium Hydroxide to pH 10.	7 days
16	Screw cap glass vial with teflon lined screw cap.	If pre-treatment necessary: Bottle: Sequence of extensive washing hot water detergent, water, distilled water. Bake at 300 C for 8 hr minimum. Cap: no pre-treatment.	Contact surfaces must be glass, teflon or stainless steel. Fill bottle slowly to top - no air space.	25 mL	Precharge bottles with 80 mg Na2SO3 per 1L for samples containing residual chlorine. Keep in the dark.	7 days

SCHEDULE 2 - SAMPLING PRINCIPLES

Column 1	Column 2	Column 3	Column 4	Col. 5	Column 6	Column 7
ANALYTIC TEST GROUP #	SAMPLE CONTAINER	CONTAINER PRE-TREATMENT	TEST SPECIFIC SAMPLING PRECAUTIONS	MIN. SAM. VOL.	PRESERVATION METHOD*	STORAGE TIME
17	Screw cap glass vial with teflon lined screw cap.	If pre-treatment necessary: Bottle: Sequence of extensive washing hot water detergent, water, distilled water. Bake at 300 C for 8 hr minimum. Cap: no pre-treatment.	Contact surfaces must be glass, teflon or stainless steel. Fill bottle slowly to top - no air space.	25 mL	Precharge bottles with 80 mg Na2SO3 per 1L for samples containing residual chlorine. Keep in the dark.	7 days
18	Screw cap glass vial with teflon lined screw cap.	If pre-treatment necessary: Bottle: Sequence of extensive washing hot water detergent, water, distilled water. Bake at 300 C for 8 hr minimum. Cap: no pre-treatment.	Contact surfaces must be glass, teflon or stainless steel. Fill bottle slowly to top - no air space.	25 mL	Precharge bottles with 80 mg Na2SO3 per 1L for samples containing residual chlorine. Keep in the dark.	7 days
19	1L Boston round, amber glass, Dominion Glass #6962 or equivalent 28 mm foil or teflon lined screw cap.	If pre-treatment necessary: Bottle: Sequence of extensive washing hot water detergent, water, distilled water. Bake at 300 C for 8 hr minimum or 3 rinses with pesticide grade or distilled in glass hexane and dichloromethane. Cap: no pre-treatment.	Contact surfaces must be glass, teflon or stainless steel.	800 mL	None	30 days

SCHEDULE 2 - SAMPLING PRINCIPLES

Column 1	Column 2	Column 3	Column 4	Col. 5	Column 6	Column 7
ANALYTIC TEST GROUP #	SAMPLE CONTAINER	CONTAINER PRE-TREATMENT	TEST SPECIFIC SAMPLING PRECAUTIONS	MIN. SAM. VOL.	PRESERVATION METHOD*	STORAGE TIME
20	1L Boston round, amber glass, Dominion Glass #6962 or equivalent 28 mm teflon lined screw cap.	If pre-treatment necessary: Bottle: Sequence of extensive washing hot water detergent, water, distilled water. Bake at 300 C for 8 hr minimum or 3 rinses with pesticide grade or distilled in glass hexane and dichloromethane. Cap: no pre-treatment.	Contact surfaces must be glass, teflon or stainless steel.	800 mL	None	30 days
21	1L Boston round, amber glass, Dominion Glass #6962 or equivalent 28 mm foil or teflon lined screw cap If analyzed on same sample as Extractables, Acid(Phenolics) cap liner must be teflon.	If pre-treatment necessary: Bottle: Sequence of extensive washing hot water detergent, water, distilled water. Bake at 300 C for 8 hr minimum or 3 rinses with pesticide grade or distilled in glass hexane and dichloromethane. Cap: no pre-treatment.	Contact surfaces must be glass, teflon or stainless steel. Fill bottle to at least 800 mL.	800 mL	None	30 days
22	1L Boston round, amber glass, Dominion Glass #6962 or equivalent 28 mm foil or teflon lined screw cap.	If pre-treatment necessary: Bottle: Sequence of extensive washing hot water detergent, water, distilled water. Bake at 300 C for 8 hr minimum or 3 rinses with pesticide grade or distilled in glass hexane and dichloromethane. Cap: no pre-treatment.	Contact surfaces must be glass, teflon or stainless steel.	800 mL	None	30 days

SCHEDULE 2 - SAMPLING PRINCIPLES

Column 1 ANALYTIC TEST GROUP #	Column 2 SAMPLE CONTAINER	Column 3 CONTAINER PRE-TREATMENT	Column 4 TEST SPECIFIC SAMPLING PRECAUTIONS	Col. 5 MIN. SAM. VOL.	Column 6 PRESERVATION METHOD*	Column 7 STORAGE TIME
23	1L Boston round, amber glass, Dominion Glass #6962 or equivalent 28 mm foil or teflon lined screw cap	If pre-treatment necessary: Bottle: Sequence of extensive washing hot water detergent, water, distilled water. Bake at 300 C for 8 hr minimum or 3 rinses with pesticide grade or distilled in glass hexane and dichloromethane. Cap: no pre-treatment.	Contact surfaces must be glass, teflon or stainless steel.	800 mL	None	30 days
24	1L Boston round, amber glass, Dominion Glass #6962 or equivalent 28 mm teflon lined screw cap or 4L Winchester, amber glass with teflon lined screw cap.	For all containers: Bottle: Sequence of extensive washing hot water detergent water, distilled water. Bake at 300 C for 8 hr minimum. or 3 rinses with pesticide grade or distilled in glass hexane and dichloromethane. Cap: no pre-treatment.	Contact surfaces must be glass, teflon or stainless steel.	1 L	None	30 days
25	1L Boston round, amber glass, Dominion Glass #6962 or equivalent 28 mm foil or teflon lined screw cap.	Container is used once only.	Contact surfaces must be glass, teflon or stainless steel.	800 mL	None	7 days

SCHEDULE 2 - SAMPLING PRINCIPLES

Column 1	Column 2	Column 3	Column 4	Col. 5	Column 6	Column 7
ANALYTIC TEST GROUP #	SAMPLE CONTAINER	CONTAINER PRE-TREATMENT	TEST SPECIFIC SAMPLING PRECAUTIONS	MIN. SAM. VOL.	PRESERVATION METHOD*	STORAGE TIME
26	1L Boston round, amber glass, Dominion Glass #6962 or equivalent 28 mm foil or teflon lined screw cap.	If pre-treatment necessary: Bottle: Sequence of extensive washing hot water detergent, water, distilled water. Bake at 300 C for 8 hr minimum or 3 rinses with pesticide grade or distilled in glass hexane and dichloromethane. Cap: no pre-treatment.	Contact surfaces must be glass, teflon or stainless steel.	800 mL	None	30 days
27	1L Boston round, amber glass, Dominion Glass #6962 or equivalent 28 mm foil or teflon lined screw cap.	If pre-treatment necessary: Bottle: Sequence of extensive washing hot water detergent, water, distilled water. Bake at 300 C for 8 hr minimum or 3 rinses with pesticide grade or distilled in glass hexane and dichloromethane. Cap: no pre-treatment.	Contact surfaces must be glass, teflon or stainless steel.	800 mL	None	30 days
					* preservation methods listed are in addition to requirements set out in Section 13 (10).	

SCHEDULE 3A - ANALYTICAL PRINCIPLES METHOD DETECTION LIMITS

COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6
ANALYTIC TEST GROUP #	PARAMETERS CONVENTIONAL AND METAL PARAMETERS	SAMPLE PREPARATION METHOD PRINCIPLES	INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	METHOD DETECTION LIMIT mg/L
1	Chemical oxygen demand (COD)	Reflux (samples with solids) or Oven digestion at 150 C in presence of redox reagents	Back titration or Colourimetric measurement of Cr III	N/A	10
2	Cyanide	Acid distillation	Colourimetry or Titration if >1mg/L	N/A	0.005
3	Hydrogen ion (pH)	None	pH electrode and pH meter	N/A	N/A
4a	Ammonia plus Ammonium	Distillation unless proven unnecessary	Colourimetry or Specific ion electrode or Titration	N/A	0.25 as N
	Total Kjeldahl nitrogen	Standard Kjeldahl digestion procedure unless proven unnecessary	Colourimetry	N/A	0.5 as N
4b	Nitrate (Analyzed directly or calculated as the difference between the total of Nitrate plus Nitrite and Nitrite)	None	Colourimetry including step for reduction of NO3 to NO2 or Automated Technicon or Ion Chromatography	N/A	0.25 as N
	Nitrite	None	Colourimetry or Titration or Automated Technicon or Ion Chromatography	N/A	0.025 as N

SCHEDULE 3A - ANALYTICAL PRINCIPLES METHOD DETECTION LIMITS

COLUMN 1 ANALYTIC TEST GROUP #	COLUMN 2 PARAMETERS CONVENTIONAL AND METAL PARAMETERS	COLUMN 3 SAMPLE PREPARATION METHOD PRINCIPLES	COLUMN 4 INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	COLUMN 5 ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	COLUMN 6 METHOD DETECTION LIMIT mg/L
5	Dissolved organic carbon	Strip inorganic carbon	Automated UV digestion plus colourimetric measurement of C02; or equivalent	N/A	0.5 as C
	Total organic carbon (TOC)	Strip inorganic carbon	Beckman TOC analyzer or equivalent	N/A	5 as C
6	Total phosphorus	Perchloric acid digestion unless proven unnecessary	Colourimetry	N/A	0.1 as P
7	Specific conductance	None	Conductivity meter and cell	N/A	5 µS/cm
8	Total suspended solids (TSS)	None	Gravimetric; particle retention of glass fibre filter < or = 1.5 micron	N/A	2
	Volatile Suspended solids (VSS)	Perform TSS analysis	Ignite filter at 550 C for 4 hr. or until filter weight remains constant.	N/A	4

SCHEDULE 3A - ANALYTICAL PRINCIPLES METHOD DETECTION LIMITS

COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6
ANALYTIC TEST GROUP #	PARAMETERS CONVENTIONAL AND METAL PARAMETERS	SAMPLE PREPARATION METHOD PRINCIPLES	INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	METHOD DETECTION LIMIT mg/L
9	Aluminum	Nitric evaporation or aqua regia digestion	Atomic absorption spectrometry and/or Inductively Coupled Plasma (ICP)	N/A	0.03
	Beryllium				0.01
	Cadmium				0.002
	Chromium				0.02
	Cobalt				0.02
	Copper				0.01
	Lead				0.03
	Molybdenum				0.02
	Nickel				0.02
	Silver				0.03
	Thallium			N/A	0.03
	Vanadium				0.03
	Zinc				0.01
10	Antimony	Acid Digestion	Hydride Generation Atomic Absorption	N/A	0.005
	Arsenic				0.005
	Selenium				0.005
11	Chromium (Hexavalent) (Analyze for hexavalent Chromium only if total Chromium >.5 mg/L)	a) None b) Solvent extraction	a) Colourimetry b) Atomic absorption	N/A	0.01
12	Mercury	Oxidative acid digestion	Cold vapour atomic absorption	N/A	0.0001

SCHEDULE 3A - ANALYTICAL PRINCIPLES METHOD DETECTION LIMITS

COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6
ANALYTIC TEST GROUP #	PARAMETERS CONVENTIONAL AND METAL PARAMETERS	SAMPLE PREPARATION METHOD PRINCIPLES	INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	METHOD DETECTION LIMIT mg/L
13	Tetra-alkyl lead Tri-alkyl lead (-inorganic ligand) (Analyze for alkyl leads only if Total lead is greater than .5mg/L)	a) Liquid/liquid extraction b) Derivatization	a) Colourimetry using Dithiozone reagent or Atomic absorption b) Gas Liquid Chromatography Atomic absorption	N/A	0.002 0.002
14	Phenolics (4AAP)	Distillation from acidified (pH<4) sample	Colourimetry (520nm) of buffered sample	N/A	0.002
15	Sulphide	Filtration and dissolution of precipitate	Methylene blue colourimetry or Specific Ion Electrode	N/A	0.02

SCHEDULE 3B - ANALYTICAL PRINCIPALS METHOD DETECTION LIMITS

COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6
ANALYTIC TEST GROUP #	PARAMETERS ORGANIC PARAMETERS	SAMPLE PREPARATION METHOD PRINCIPLES	INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	METHOD DETECTION LIMIT µg/L
16	1,1,2,2-Tetrachloroethane	Purge and trap	Gas Chromatography/ Mass Spectrometry (GC/MS)	Gas Chromatography/ Electron Capture or Hall Single capillary column	10
	1,1,2-Trichloroethane				10
	1,1-Dichloroethane				10
	1,1-Dichloroethylene				10
	1,2-Dichlorobenzene				10
	1,2-Dichloroethane (Ethylene dichloride)				10
	1,2-Dichloropropane				10
	1,3-Dichlorobenzene				10
	1,4-Dichlorobenzene				10
	Bromoform				10
	Bromomethane				ND
	Carbon tetrachloride				10
	Chlorobenzene				10
	Chloroform				10
	Chloromethane				ND
	Cis-1,3-Dichloropropylene				10
	Dibromochloromethane				10
	Dichlorobromomethane				10
	Ethylene dibromide				10
	Methylene chloride				10
	Tetrachloroethylene (Perchloroethylene)				10
	Trans-1,2-Dichloroethylene				10
	Trans-1,3-Dichloropropylene				ND
	Trichloroethylene				10
	Trichlorofluoromethane				10
	Vinyl chloride (Chloroethylene)				ND

SCHEDULE 3B - ANALYTICAL PRINCIPALS METHOD DETECTION LIMITS

COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6
ANALYTIC TEST GROUP #	PARAMETERS ORGANIC PARAMETERS	SAMPLE PREPARATION METHOD PRINCIPLES	INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	METHOD DETECTION LIMIT µg/L
17	Benzene	Purge and trap	Gas Chromatography/ Mass Spectometry (GC/MS)	Gas Chromatography Flame Ionization or Photo Ionization Single capillary column	10
	Ethylbenzene				10
	Methyl ethyl ketone				10
	Styrene				10
	Toluene				10
	o-Xylene				10
	m-Xylene/p-Xylenes				10
18	Acrolein	Purge and trap	Gas Chromatography/ Mass Spectrometry (GC/MS)	Gas Chromatography Electron Capture/Hall & Flame Ionization/ Photo Ionization Single capillary column	ND
	Acrylonitrile				ND
	1,3-Butadiene				ND

SCHEDULE 3B - ANALYTICAL PRINCIPALS METHOD DETECTION LIMITS

COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6
ANALYTIC TEST GROUP #	PARAMETERS ORGANIC PARAMETERS	SAMPLE PREPARATION METHOD PRINCIPLES	INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	METHOD DETECTION LIMIT µg/L
19	Acenaphthene	Liquid/liquid extraction	Gas Chromatography/ Mass Spectrometry (GC/MS)	High Performance Liquid Chromotography UV of Fluorescene Detection	10
	5-nitro Acenaphthene				10
	Acenaphthylene				10
	Anthracene				10
	Benz(a)anthracene				10
	Benzo(a)pyrene				10
	Benzo(b)fluoranthene				10
	Benzo(ghi)perylene				10
	Benzo(k)fluoranthene				10
	Camphene				10
	1-Chloronaphthalene				10
	2-Chloronaphthalene				10
	Chrysene				10
	Dibenz(a,h)anthracene				10
	Fluoranthene				10
	Fluorene				10
	Indeno(1,2,3-cd)pyrene				10
	Indole				ND
	1-Methyl naphthalene				10
	2-Methyl naphthalene				10
	Naphthalene				10
	Perylene				10
	Phenanthrene				10
	Pyrene				10

SCHEDULE 3B - ANALYTICAL PRINCIPALS METHOD DETECTION LIMITS

COLUMN 1 ANALYTIC TEST GROUP #	COLUMN 2 PARAMETERS ORGANIC PARAMETERS	COLUMN 3 SAMPLE PREPARATION METHOD PRINCIPLES	COLUMN 4 INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	COLUMN 5 ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	COLUMN 6 METHOD DETECTION LIMIT µg/L
19 cont'd	Benzyl butyl phthalate	Liquid/liquid extraction	Gas Chromatography/ Mass Spectrometry (GC/MS)	N/A	10
	Bis(2-ethylhexyl)phthalate				10
	Di-n-butyl phthalate				10
	Di-n-octyl phthalate				10
	4-Bromophenyl phenyl ether				10
	4-Chlorophenyl phenyl ether				10
	Bis(2-chloroisopropyl)ether				10
	Bis(2-chloroethyl)ether				10
	Diphenyl ether				10
	2,4-Dinitrotoluene				10
	2,6-Dinitrotoluene				10
	Bis(2-chloroethoxy)methane				10
	Diphenylamine				10
	N-Nitrosodiphenylamine				10
	N-Nitrosodi-n-propylamine				10

SCHEDULE 3B - ANALYTICAL PRINCIPALS METHOD DETECTION LIMITS

COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6
ANALYTIC TEST GROUP #	PARAMETERS ORGANIC PARAMETERS	SAMPLE PREPARATION METHOD PRINCIPLES	INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	METHOD DETECTION LIMIT µg/L
20	2,3,4,5-Tetrachlorophenol	Liquid/liquid extraction pH adjusted to <2 Derivatization Cleanup	Gas Chromatography/ Mass Spectrometry (GC/MS)	N/A	10
	2,3,4,6-Tetrachlorophenol				10
	2,3,5,6-Tetrachlorophenol				10
	2,3,4-Trichlorophenol				10
	2,3,5-Trichlorophenol				10
	2,4,5-Trichlorophenol				10
	2,4,6-Trichlorophenol				10
	2,4-Dimethyl phenol				10
	2,4-Dinitrophenol				10
	2,4-Dichlorophenol				10
	2,6-Dichlorophenol				10
	4,6-Dinitro-o-cresol				10
	2-Chlorophenol				10
	4-Chloro-3-methylphenol				10
	4-Nitrophenol				10
	m-Cresol				10
	o-Cresol				10
	p-Cresol				10
	Pentachlorophenol				10
	Phenol				10
21		Liquid/liquid extraction pH adjusted to <2 Derivatization Cleanup	Gas Liquid Chromatography Electron capture Dual capillary	N/A	

SCHEDULE 3B - ANALYTICAL PRINCIPALS METHOD DETECTION LIMITS

COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6
ANALYTIC TEST GROUP #	PARAMETERS ORGANIC PARAMETERS	SAMPLE PREPARATION METHOD PRINCIPLES	INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	METHOD DETECTION LIMIT µg/L
22		Liquid/liquid extraction Neutral pH Cleanup	Gas Liquid Chromatography Electron capture Dual capillary	N/A	
23	1,2,3,4-Tetrachlorobenzene	Liquid/liquid extraction Neutral pH Cleanup if necessary	Gas Liquid Chromatography Electron capture Dual capillary	N/A	0.01
	1,2,3,5-Tetrachlorobenzene				0.01
	1,2,4,5-Tetrachlorobenzene				0.01
	1,2,3-Trichlorobenzene				0.01
	1,2,4-Trichlorobenzene				0.01
	2,4,5-Trichlorotoluene				0.01
	Hexachlorobenzene				0.01
	Hexachlorobutadiene				0.01
	Hexachlorocyclopentadiene				0.01
	Hexachloroethane				0.01
	Octachlorostyrene				0.01
	Pentachlorobenzene				0.01
24	2,3,7,8-Tetrachlorodibenzo-p-dioxin	Liquid/liquid extraction and cleanup	Gas Chromatography/ Mass Spectroscopy (GC/MS)	N/A	0.0003
	Octachlorodibenzo-p-dioxin				0.0003
	Octachlorodibenzofuran				0.0003
	Total heptachlorinated dibenzo-p-dioxins				0.0003
	Total heptachlorinated dibenzofurans				0.0003
	Total hexachlorinated dibenzo-p-dioxins				0.0003
	Total hexachlorinated dibenzofurans				0.0003
	Total pentachlorinated dibenzo-p-dioxins				0.0003
	Total pentachlorinated dibenzofurans				0.0003
	Total tetrachlorinated dibenzo-p-dioxins				0.0003
	Total tetrachlorinated dibenzofurans				0.0003

SCHEDULE 3B - ANALYTICAL PRINCIPALS METHOD DETECTION LIMITS

COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6
ANALYTIC TEST GROUP #	PARAMETERS ORGANIC PARAMETERS	SAMPLE PREPARATION METHOD PRINCIPLES	INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	METHOD DETECTION LIMIT µg/L
25	Oil and Grease	Acidify with a mineral acid to approximately pH 2 Liquid/liquid extraction	Gravimetric Weigh to + or - 5%	N/A	1000
26		Liquid/liquid extraction pH adjusted to <2 Derivatization Cleanup	Gas Liquid Chromatography Flame Ionization Detector Dual capillary	N/A	
27	PCB's (ID aroclors present & total conc)	Liquid/liquid extraction Neutral pH Cleanup if necessary	Gas Liquid Chromatography Electron capture Single capillary column	N/A	0.1
				*ND: NOT DETERMINED	

SECTION II

Explanatory Notes

to

The Draft Regulation Made Under the

Environmental Protection Act

Petroleum Refinery Effluent

EXPLANATORY NOTES TO THE DRAFT REGULATION MADE UNDER THE ENVIRONMENTAL PROTECTION ACT PETROLEUM REFINERY EFFLUENT

INTRODUCTION

The goal of the Municipal-Industrial Strategy for Abatement (MISA) Program is the improvement of Ontario's water quality through the reduction of all waste loadings and the virtual elimination of persistent toxic contaminants from waste streams discharging directly into the surface waters of the province through application of regulations under Section 136 of the Environmental Protection Act.

The first phase of the regulatory program, for each industrial sector, is the implementation of a monitoring regulation developed with industry and public input. This monitoring regulation will require self-monitoring of point source aqueous discharges to the natural environment, by all plants within the industrial sector.

The objective of the Monitoring Regulation is the establishment of a data base on effluent quality, with emphasis on toxic contaminants, reflecting all operating conditions, including normal and upset conditions, within a standardized framework of sampling, analysis, quality assurance and quality control (QA/QC), and Ministry audit.

The data will be evaluated and applied to the development and implementation of effluent limits, based on Best Available Technology Economically Achievable (BATEA), which will be included in an amendment to the Regulation. It is expected that monitoring requirements will be altered at the time of that amendment to reflect the experience gained under the Effluent Monitoring Regulation. A **listing/delisting mechanism** for this industrial sector will have been developed in the interim period to provide for the analysis of additional polllutants of concern, and/or to relieve the industry of analytical burdens which are of no further benefit.

The process laid down in the MISA White Paper, June 1986 was followed to develop the Regulation. Federal/Provincial Working Groups were formed to provide the multidisciplinary scientific technical support required. A

Joint Industry/Government Technical Committee with representatives from the federal and provincial governments and the petroleum industry (aided by the Working Groups), reviewed the technical data and industry information and came to agreement on the draft Regulation. The **MISA Advisory Committee**, reporting to the Minister, was set up to provide an independent review of the regulatory program. Its membership is drawn from knowledgeable members of the public. The very sizeable amount of information and data which these activities generated, collected, compiled, analyzed, and reported upon (in the form of reports, reference documents, committee minutes, etc.) will be made available for public review.

The petroleum refining sector in Ontario is relatively homogeneous. The operation of refineries, including process descriptions and products, is well documented and understood. Although their processing rearranges the structure of hydrocarbon molecules, it does not involve the addition of other substances (such as chlorine) to feedstocks to create entirely dissimilar derivatives. It is therefore logical to assume that studies carried out at selected refineries may be applicable to other similar operations, within limits.

The Ministry recognizes the substantial accomplishments of the petroleum industry in pollution control. Secondary (biological) treatment, dissolved air flotation and oily water separation have been installed, bringing the refineries very close to BATEA as defined for petroleum refineries by the Environmental Protection Agency in the United States (USEPA). These factors, along with the availablility of the data described below, were primary considerations in the Ministry's decision to formulate regulations for the refinery sector first and to use those regulations as a framework for the other sectors.

Through the efforts of the Ontario Petroleum Association (OPA), the Petroleum Association for Conservation of the Canadian Environment (PACE) and Environment Canada, there is a significant quantity of historical and current monitoring data available from short term studies upon which to base the monitoring regulation. While the short term studies have been essential to the development of practical regulations, the data are not sufficient to achieve the objective of the Effluent Monitoring Regulation.

Four PACE studies, conducted between 1980 and 1984, were designed using experience gained and data produced from studies by the American Petroleum Institute (API) in the United States. USEPA analytical methods were generally used to determine the presence, absence and concentrations of a subset of the USEPA Priority Pollutants (the list of 129 'Consent Decree' pollutants) in selected Canadian refinery effluents. In addition three supporting reviews on chemical pollutants were done. This information base has been summarized and reviewed in a PACE document number 85-8 titled "A Survey of Trace Substances in Canadian Oil Refinery Wastewaters and Sludges--A Summary Report" . The toxicity and carcinogenicity of refinery effluents have also been studied and reported by PACE in their report number 85-4 titled "The Investigation of the Potential Carcinogenic Activity of Oil Refinery Effluents" .

A more recent supplementary study, "Sampling and Analysis of Refinery Effluents to Assess Variations in Trace Contaminant Concentrations" (January, 1987), was completed during the pre-regulatory period. Effluent variability at two Ontario refineries was studied under the supervision of the Joint Government-Industry Technical Committee for the Refineries sector. The Committee also reviewed the historical PACE and OPA data in a report entitled: "Environmental Contaminants in Petroleum Refinery Waste Waters: An Assessment of Current Information and a Monitoring Approach (July 1987). Copies of both reports are available from the Ministry upon request.

The MISA program will extend these short term studies over a range of operating conditions and seasons to determine the long term effects of persistent toxics.

Other industrial sectors in Ontario have not placed in the public domain equivalent studies on the priority pollutants in their effluents. They may be required to supply more information on their effluents during the pre-regulatory phase and to do more monitoring under regulation. The monitoring regulation for this industrial sector will, however, provide the framework on which to base the regulations for other industrial sectors.

APPLICATION OF REGULATION

The petroleum refinery sector is easily defined in Ontario and is limited to seven refineries, all of which discharge to the Great Lakes system. Section 2 of the Regulation classifies these seven refineries as effluent dischargers of the "petroleum refinery class". The Regulation applies only to that class. Future refineries will be made subject to the Regulation through amendment.

With the exception of initial reporting of process information [Section 15 (1)], the Regulation will come into force six months after promulgation. This six month period will allow time for the purchase and installation of equipment and the training of staff.

The quarterly and three times weekly monitoring of process effluents as specified in Sections 6 and 7 will only be required for a period of twelve months. The monitoring of once through cooling water, storm water, emergency overflows, and landfarm leachates, as specified in this Regulation, will cease after 12 months. As stated, a **listing/delisting mechanism** will be developed during that period. A more customized form of monitoring will be continued by amendment to the Regulation.

The Regulation will also be amended to include effluent limits when they are established.

CHARACTERIZATION

Section 4 of the Regulation sets out the requirements for characterization for a list of pollutants of concern. This list, specified in Column 2 of Schedule 1, is based on the initial Effluent Monitoring Priority Pollutants List (EMPPL) and includes conventional parameters. Appendix A presents a comparison of the EMPPL parameters and the Petroleum Refinery characterization parameters. The rationale and procedures employed by the Ministry to prepare the EMPPL are described at length in a document entitled "Development of an Effluent Monitoring Priority Pollutants List" June, 1987.

The priority pollutants on the Petroleum Refinery characterization list are a subset of EMPPL and include those chemicals for which documented and validated analytical methods are available. Validated cost-effective methods will be developed and documented on a priority basis for chemicals included on EMPPL but not on the refinery characterization list. Pollutants which are not in any way likely to arise from refinery operations (such as the resin and fatty acids acids associated with pulp and paper effluents) are excluded from the refinery sector list but may be listed at some future date if characterization suggests their presence. The data from previous studies have been used to assign subsets of the refinery sector list to various levels of monitoring frequency based on the likelihood of release, relevance to treatment or process control, or potential environmental significance.

Many of the pollutants in Schedule 1 are not expected to be in treated petroleum refinery effluent, but characterization permits the establishment of a long term data base within a uniform regulatory framework. The detection of a priority pollutant not previously reported in petroleum refinery effluents may trigger more frequent monitoring, if warranted, through inclusion of the pollutant on routine monitoring lists.

The purpose of characterizing effluent discharges is to determine the presence or absence of pollutants of concern in petroleum refinery effluent, following consistent and uniform sampling and analytical principles and protocols.

Characterization will be an **ongoing requirement** to ensure that there are no significant changes in the quality of the effluent over time.

Characterization is required initially (ie. within 3 months of first routine sampling) once between six and nine months later, every three years thereafter, and after each significant process change. A significant process change is defined as any change in process, treatment, or plant and sewer layout which may adversely affect effluent quality, and/or for which the discharger would normally require application to the Ministry for a Certificate of Approval.

Characterization of all process effluent streams will occur at defined **sampling locations** following final treatment but prior to dilution with once through cooling water.

The sampling requirements are set out in Section 13 and in Schedule 2. The requirements for laboratory analysis of samples are set out in Section 14 and Schedule 3. A more complete description is provided under the headings 'Sampling Requirements' and 'Analytical Requirements'.

In view of the previous characterization studies on refinery effluents and the nature of the refinery processes referred to in the Introduction Section, dischargers in the refinery class are required to perform **'closed' characterization** (ie. for a specified list.)

The Ministry of the Environment will perform **'open-ended' characterization** on effluent samples, as an integral part of its audit program. Gas chromatography/mass spectrometry analyses will be performed to identify and quantify all organic compounds present at state-of-the-art detectable concentrations as compared to an internal standard (eg. as close to 1 microgram per litre as possible depending upon the specific analyte and the sample matrix). Compounds will be identified using a computerized library search of approximately 30,000 mass spectra listings, at greater than 80% match, and through manual interpretation by experienced analysts. In addition, elemental scans will be performed for metals, other than those for which monitoring is already required, and other elements present at significant levels.

The Ministry recognizes that further research is required and is planning to pursue further development in several areas such as:

a) To identify in refinery effluents, specific analytes, within the analytical groups of alkylated polyaromatic hydrocarbons, mercaptans, thiophenes, ketones, and alkylated phenolics, at state-of-the-art detection levels. The actual levels will depend upon the analyte and the matrix, but will likely be in the order of 1 microgram per litre for most analytes.

b) To assess the specific chemicals identified in the refinery effluents, through the research studies, by means of the Hazard Assessment Screen (the screening procedure employed in developing the EMPPL) and add them to the EMPPL as warranted.

c) To develop standard, cost-effective, analytical methods to quantify alkylated PAHs and other chemicals of interest on a priority basis.

The Ministry will then be in a position to **amend the characterization** list for refineries based upon this information.

ROUTINE MONITORING

The requirements for routine chemical monitoring are set out in Sections 5 through 10. Sampling and analytical requirements are set out in Section 13 (Schedule 2) and Section 14 (Schedule 3) respectively.

Process effluent streams will be monitored at a point following final treatment, but prior to dilution, as follows:

On a **daily basis,** Section 5 requires dischargers to monitor for total phenolics (4AAP); volatile suspended solids; and pH. These parameters are 'indicator' or 'surrogate' parameters, which monitor process and treatment variables. These surrogates may provide a cost effective assessment of treatment efficiency and hence effluent quality.

Three times per week, Section 6 requires dischargers to monitor for ammonia nitrogen; total organic carbon; total phosphorus; total suspended solids; sulphide; benzene; toluene; o-xylene; m-xylene and p-xylene; ethylbenzene; oil and grease; and chromium and zinc (where these are used in the treatment of cooling water). The purpose of this monitoring is to provide a sound data base on the discharge of selected conventional and priority pollutants. These pollutants are always present in untreated process wastewater from petroleum refineries and are of environmental significance. They will be assessed as candidates for the setting of effluent limits by amendment to the regulation.

Quarterly, in clusters of 3 daily samples taken within a single week, Section 7 requires dischargers to monitor for a longer list of pollutants, (set out in Column 6 of Schedule 1). The purpose of quarterly monitoring is to establish a data base for twenty groups of pollutants from the characterization list, selected because they are known to be present or likely to be present in petroleum refinery effluent. The selected compounds are usually at low concentrations in final effluents, but have been frequently detected in significant concentrations in wastes prior to biotreatment. The concentrations in final effluents may therefore fluctuate and be environmentally significant over the long term. Quarterly cluster monitoring has advantages of providing more than one result, in a short time-span on a seasonal basis for each parameter, and thus increasing statistical significance, simplifying the logistics of sampling and transportation, and potentially reducing sampling and analytical costs where contract laboratories are used.

In addition to the more frequently monitored parameters, the quarterly monitoring list consists of chemical oxygen demand; cyanide; dissolved organic carbon; specific conductance; chromium (hexavalent); mercury; and all characterization parameters in the following analytical groups: Nitrogen; Total metals; Total alkyl lead; Hydrides; Volatiles, halogenated; Volatiles, non-halogenated; and Extractables, acid phenolics. Only the Polynuclear Aromatic Hydrocarbons from the Extractables, base neutral analytical test group, are included.

The Volatiles, halogenated analytical test group is included in the 'quarterly' monitoring list because these chemicals have been detected in refinery effluent. It is recognized that these chemicals may be detected in effluent samples for any of three reasons: presence in the intake water; addition of chlorine to cooling water; and laboratory artifacts. Halogenated volatiles, present in intake water and discharged in final effluent, may cause an exceedance of Ministry receiving water objectives downstream from the refinery. Chlorine is also occasionally used to control slime growth in refinery cooling water, possibly leading to chlorinated organic formation where there is contact with contaminated streams. There appears to be some uncertainty as to whether the frequently reported detection of group members such as methylene chloride, carbon tetrachloride and chloroform in both American Petroleum Institute and PACE studies is an artifact of laboratory contamination. The Quality Assurance and Quality Control requirements set out in this Regulation are intended to monitor the impact of this problem.

Quarterly monitoring will provide data on the polynuclear aromatic hydrocarbons (PAH's), in the Extractables, base neutral analytical test group, which have traditionally caused concern in effluents from this sector. Other PAH's present in refinery effluent, in particular methylated PAH's, have been identified by PACE and other reviews as potentially carcinogenic and hence an environmental concern. The methylated PAH compounds appear to be more typical of refinery effluents than the more familiar carcinogens such as benzo-(a)-pyrene. However, little is known about the specific analytes and the concentrations of these PAH's. The Ministry recognizes that the development of standard, cost-effective analytical methods will be needed to quantify the methylated PAH's; however, proven methods for routine monitoring are not expected to be available during the initial 12 month monitoring period of the Regulation.

Phthalates from Group 19 were considered for inclusion in the petroleum refining monitoring regulation because they have been reported in refinery effluent samples. Accordingly, they have been included on the refinery characterization list and the Ministry effluent audit program, but have not been included in the quarterly monitoring program. Available data in the literature (1, 2) indicates that the detection of phthalates at low levels in refinery effluent samples is most likely an artifact of the sampling and analytical methodology. Many analyses of refinery intake and effluent samples in the current data base have not shown any consistent difference which would dispute this conclusion. (References:1. PACE Report No. 85-6: Evaluation of the Variability of Trace Organic Substances in Petroleum Refining Effluents, 2. CanViro, January 21, 1987: Sampling and Analysis of Refinery Effluents to Assess Variations in Trace Contaminant Concentrations). Furthermore, the analysis requires the GC/MS technique and frequent analysis could not be justified as worthwhile utilization of a very limited resource. Other compounds from Group 19 were not included because they were not detected or expected from refinery processes.

The initial review of data indicated that chemicals from analytical test group 18 were not present. However, new information indicates the potential presence of acrolein, and therefore this group should be considered for quarterly monitoring. The Ministry will resolve this prior to the regulation being promulgated.

Chemicals from the analytical test groups 23 (Extractables, neutral chlorinated); 24 (Dioxins and Furans); 26 (Fatty and Resin Acids); and 27 (PCB's) were not included under quarterly monitoring. These chemicals are not expected from refinery processes and with the exception of Hexachorobenzene (HCB) have not been reported in effluents. HCB from group 23 was reported at levels marginally above the detection limit; however it was also present at the same levels in intake waters. These groups will be monitored by the refineries as part of characterization and by the Ministry as part of the audit program.

The data base obtained from quarterly monitoring will be used to:

a) Establish the relationships, if any, between the shorter list of chemicals monitored frequently and the longer list of chemicals monitored less frequently for the purpose of optimizing the monitoring list of parameters and frequency of sampling and analysis.

b) Provide supporting data for toxicity testing performed on samples taken concurrently.

c) Provide a preliminary indication of the amount and variability of annual loadings.

d) Compare quarterly loading estimates against the 30 day average loading estimates with a view to reduce sampling frequency wherever possible.

e) Investigate correlations with trend data from receiving water programs such as the 'in place pollutants' (sediment analysis) and fish programs.

Once through cooling water streams will be monitored once per month, as set out in Section 8, for pH; total organic carbon; total phosphorus; total and volatile suspended solids; phenolics (4AAP); sulphide; benzene; toluene; o-xylene; m-xylene and p-xylene; ethylbenzene; and oil and grease. The purpose of monitoring cooling water for these parameters is the detection of low level process losses over the long term which may result in significant contaminant loadings.

Potentially contaminated **storm water and emergency overflows** of incompletely treated process effluent caused by precipitation will be monitored as set out in Section 9 for pH; ammonia nitrogen; total organic carbon; total phosphorus; total and volatile suspended solids; chromium and zinc (where used); phenolics (4AAP); sulphide; benzene; toluene; o-xylene; m-xylene and p-xylene; ethylbenzene; oil and grease. The sample must be taken near the beginning of each discharge. Overflows of incompletely treated process effluent caused by major storms are known to contribute significant contaminant loadings to surface waters.

Each planned direct discharge to a receiving water course of **landfarm leachate** (which does not receive treatment), will be monitored as set out in Section 10 for the three times weekly list. At least once per year direct leachate discharges must also be monitored for the quarterly list. Leachate discharges to surface water are currently subject to monitoring conditions on Certificates of Approval under Part V of the Environmental Protection Act which do not include priority pollutants.

TOXICITY TESTING

Section 11 of the Regulation requires effluent dischargers to monitor for **acute lethality to fish** (Rainbow Trout), applying the static 96 hour LC50 toxicity test described in the Ministry of the Environment document "Protocol to Determine the Acute Lethality of Liquid Effluents to Fish", July 1983.

Ontario applies the static 96 hour acute lethality test as a simple and relatively cost-effective 'first level of protection' test. A graded concentration (water/waste) series is used to establish the concentration of effluent allowing 50% survival in a test population of Rainbow Trout fingerlings (ie. the LC50 concentration.)

Courts have generally recognized fish mortality in laboratory testing as evidence of the capacity of a liquid effluent to impair receiving water, even in the absence of proof that there is a demonstrated effect of similar magnitude in the actual environment. The Rainbow Trout Test is currently the standard lethality test in Ontario. A similar test is applied as a pass-fail test in the federal Petroleum Refinery Effluent Regulations and Guidelines under the Fisheries Act.

The Ministry has accepted a MISA Advisory Committee recommendation, supported by other reviewers and the global literature, to require the performance of a **48 hour Daphnia magna immobilization test** in addition to the standard fish test. The petroleum refinery representatives have agreed to the proposal subject to validation of a Ministry protocol expected to be available prior to promulgation of the regulation. Validation of a protocol would normally include peer review and 'round-robin' testing involving several laboratories and agencies. The restrictive time-frame may not allow completion of a test cycle.

The Daphnia testing requirement has **not** been included in the **regulation text** at this time prior to the availablity of details about sampling and testing methodolgy and discussion with the industry members of the Joint Technical Committee. The test is more sensitive, requires greater dilution of the effluent sample and hence lesser sample volumes. While details remain to be finalized, it is expected that the test will be performed on a sub-sample of the fish-test sample at the same frequency. The Ministry has also committed itself to accelerated review and development of

continuous flow testing of effluents to futher increase sensitivity. There are less severe logistic difficulties associated with performing such tests on Daphnia.

The tests are to be performed on a monthly basis with a sample collected from each process effluent sampling point (i.e. after final treatment but before dilution with once through cooling water) and on a quarterly basis with a sample collected from each cooling water sampling point. The application of toxicity testing to undiluted treated process effluent samples represents a more stringent requirement than in the past.

Toxicity testing usually refers to the testing of the effects of an effluent or constituents of an effluent on aquatic biota before the effluent has had a chance to be assimilated in receiving waters. The testing is therefore preemptive. Effluents which are expected to pass the static 96 hr. LC50 toxicity test are not likely to have measurable environmental impacts after dilution in the receiving water; effluents which do not pass the test may have impacts depending upon the available dilution and the nature of the toxic substances in the waste. Since toxicity testing integrates the effects of all waste parameters whether their presence is suspected or not, it complements the specific chemical testing required under routine monitoring.

Effluents which are expected to pass the static 96 hr. LC50 toxicity test (eg. once-through cooling water) are tested on a less frequent, single-concentration, pass-fail basis unless lethality is observed in the undiluted effluent, when additional concentrations and potentially more frequent testing may be required.

Acute lethal testing, while not capable of predicting chronic effects or bioaccumulation, is a useful form of testing for regulatory purposes. More sophisticated testing introduces greater uncertainty to the prediction of an effect after dilution. Appropriate chronic toxicity testing would be useful to detect and quantify subtle, long-term problems caused by these treated effluents. However, until standard protocols and interpretation techniques are developed, chronic toxicicty testing on a site specific basis is best left to water quality evaluations. Evaluations of chronic testing are currently underway in the Ministry of the Environment Laboratories with more sensitive species, such as water fleas (Daphnia spp), and with more than one life stage of test fish.

The **monthly testing** of undiluted treated process effluents and the **quarterly testing** of less contaminated waste streams are reasonable frequencies for the establishment of a data base to be applied to the development of regulatory limits.

Consideration will be given to reducing the test frequency if emerging data consistently shows no acute toxicity.

FLOW MEASUREMENT

Accurate flow measurement is essential to the determination of contaminant loadings to surface watercourses. Section 12 of the Regulation requires the measurement and recording of flow at the sampling points for process effluent, once through cooling water, and storm water.

The flow rates of **process effluent streams** (ie. after final treatment but before dilution) must be measured continuously using flow measuring systems, such as those referred to in Appendix B, adhering to the principles described below.

> **Flow measuring systems** in most instances consist of a primary measuring device to establish the relationship between flow rate and a measured variable, and a secondary measuring device, to convert the measured variable to a flow rate in volumetric units per unit time.
>
> **Primary measuring devices** as defined in the Regulation and when properly installed and operating within their defined operating range are accurate to plus or minus 5% of the true rate. **Secondary devices** as defined in the Regulation are capable of plus or minus 2% (relative value) of full scale or better. The combined accuracy of the system for process effluents must therefore be within plus or minus 7% of actual flow rate at fullscale but no worse than plus or minus 15% of actual flow rate for the defined design range of the measuring system.
>
> For example, sharp crested weirs and orifice plates are primary devices which have uniquely defined relationships between flow over the weir and water level at the gauging point in the former case, and flow through the orifice and differential pressure across the plate in the latter case. A water level or stage measuring device and a manometer or other differential pressure measuring device is a secondary device and is used to determine flow rate and the measured variable. Often ancillary devices, such as signal processors, integrators, recorders, data loggers or computers, form part of the secondary measuring device and are used to facilitate or enhance the display of information.

As a minimum, the flow rates at **cooling water and storm water** sampling points must be measured at the time of sampling. The use of water balance calculations and pumping rates is permissible provided that they are capable of accuracies of plus or minus 20% of actual flow rate verified by on-site calibration.

As a minimum, the volume and duration of discharge at landfarm leachate sampling points must be measured for each discharge of landfarm leachate to a surface water course. The use of pond drawdown and pumping rates is permissible provided that volume can be determined with an accuracy of plus or minus 20% of actual volume.

Flow measuring instruments must be regularly **maintained and calibrated.** Records of maintenance and calibration must be retained for inspection by Ministry staff.

In **Appendix B:**

> Flow measurement devices in column 1 have been chosen from various source documents and represent the majority of techniques used for effluent monitoring. Column 2 lists the outfalls for which the various methods and devices are most applicable.
>
> Column 3 details the requirements for proof of calibration to meet Section 12.-(8) of the Regulation for various methods and devices. Column 3a) and 3b) are meant to represent calibrations normally requested from the equipment supplier or independent testing laboratory at the time of purchase. For Example, a "wet test calibration certificate" can be requested from a magnetic flowmeter manufacturer for the primary element and a calibration report (using a suitable simulator of known high accuracy) can be requested for secondary devices. Column 3c) indicates those methods and devices where off-site tests may be unreliable and have to be confirmed on the actual installation or where primary devices are not applicable.
>
> Primary measurement devices not requiring proof of calibration are those that have been tested for accurate performance and accepted by various Standards Organizations/Institutions. These devices will be deemed to perform accurately if installed according to the

specifications and guidelines contained in the applicable Standard document.

SAMPLING REQUIREMENTS

The **sampling requirements** for all sampling locations described under Section 4 (characterization) and Sections 5 through 10 (routine monitoring) are specified in Section 13 and Schedule 2. Sample container, container pre-treatment, sampling precautions, minimum sample volume, preservation method, and storage time are specified for each analytical test group.

At **process effluent sampling points,** samples must be taken by one of the following specified techniques:

1) At sampling points with **variable flow**, composite samples for all parameters except sulphides, volatiles, and oil and grease must be taken over a 24 hour period using an automatic flow-proportioning composite sampling device or by manually combining, in proportion to flow, a minimum of eight grab samples taken at equal time intervals.

2) At sampling points with **relatively stable flow**, composite samples for all parameters except sulphides, volatiles, and oil and grease must be taken over a 24 hour period as described in 1) above or alternatively using an automatic equal time, equal volume composite sampling device or by manually combining a minimum of eight equal volume grab samples taken at equal time intervals.

3) For sulphides, volatiles, and oil and grease, three equal volume grab samples must be taken at intervals of at least 6 hours over a 24 hour period. These are combined at the laboratory prior to analysis.

For **cooling water sampling points**, composite samples must be prepared by combining three equal volume grab samples taken at intervals of at least 6 hours over a 24 hour period. Alternatively, samples may be taken as outlined for process effluent sampling points.

At **storm water sampling points and emergency overflows**, a single set of grab samples must be taken.

For batch discharges of **landfarm leachate**, a single set of grab samples must be taken.

All samples must be cooled immediately to between $4^{o}C$ and $10^{o}C$ by either refrigeration or through the use of ice baths and stored at that temperature until analysed. The maximum storage time for each analytical test group is specified in Column 7 of Schedule 2.

The Sampling Principles set out in Section 13 and Schedule 2 for each analytical test group are based upon the practices employed by the Ontario Ministry of the Environment, Environment Canada, and the USEPA.

Samples must be taken at an appropriate location and point within the effluent stream to ensure that the sample is representative of the effluent stream. Representative sampling locations will be chosen where effluent is turbulent or homogeneous, and where the general characteristics of the stream, such as velocity and turbulence, critical points of water quality degradation, and required accuracy of flow measurement are reflected. Also of importance in selecting sampling locations are convenience, accessibility, and practicability. The precise sampling locations on each effluent stream will be determined by the Ministry in consultation with the industry, outside the regulation.

The Ministry of the Environment cautions dischargers who clean and reuse sampling containers. Contamination of samples may result from improperly cleaned sampling equipment and containers and may lead to false positives or artificially elevated results. It is the responsibility of the discharger to ensure that sample containers are clean and free of the analytes of interest and any interferences at the time of sampling.

The quality of environmental data is affected by five basic factors: level of the contaminant, sample collection, sample preservation, analysis, and recording. The results of the sample analyses are only as good as the sampling and sample preservation techniques employed. Hence a critical component of any monitoring or regulatory program must reflect, to the greatest extent possible, the chemical, biological and/or physical properties of the effluent stream over a 24 hour period (normally 8:00 a.m. to 8:00 a.m. for practicality).

Valid, accurate, and consistent monitoring procedures will be necessary to build a uniform provincial data base composed of chemical loadings for the petroleum refinery industry discharges. After effluent limits are established, accurate data will be critical for assessing compliance.

General principles rather than specific sampling procedures and techniques are specified in the regulation to permit the flexibility required for implementation on a site to site basis.

Section 13 also requires the collection of **quality control samples** from process effluent sampling points. Each effluent discharger must collect specified quality control samples as follows: once per month for parameters analyzed daily and/or three times weekly; once per quarter for the additional parameters analyzed quarterly. The results of these samples are to be reported at the same time as the results of the routine monitoring samples.

ANALYTICAL REQUIREMENTS

The Analytical Requirements for all samples collected under characterization (Section 4), and routine monitoring (Sections 5 through 10) are set out in Section 14 and Schedule 3 of the Regulation. Alternate Analytical Instrumental Measurement Method Principles apply to routine monitoring only.

Principles of analytical methodologies, including quality assurance and quality control, specified for each analytical test group listed in Schedule 1, are based upon the analytical procedures employed by the Ontario Ministry of the Environment, Environment Canada, and the USEPA. Within the schedules, well recognized state-of-the-art sample preparation and instrumental measurement techniques (and alternates, where acceptable) are specified. The method detection limit (MDL) for each parameter is shown in Schedule 3. Parameter specific MDLs will be determined for the Volatiles and the Extractables, Base Neutral and Acid (Phenolics) using industry and Ministry generated data through the procedure outlined in the USEPA Federal Register, CFR 40, October 26, 1984, Appendix B. These MDLs will replace the interim values listed in Schedule 3 within 5 months of the date of promulgation of the Regulation.

Monitoring data for the MISA program may be generated by a number of different laboratories. The data received by the Ontario Ministry of the Environment must be reliable, of a consistant quality, and sufficiently compatible to be integrated into a valid and meaningful data base.

Many methods are available for the analysis of any given chemical substance, each of which can contribute a different bias to a given analytical result. Clearly defined analytical approaches and principles are specified for the MISA program to minimize the variability of data quality and to assist in data evaluation, interpretation, and comparison. Analytical principles for well recognized analytical techniques are specified for sample analyses as opposed to detailed, step by step analytical procedures to allow some flexibility for scientific discretion in the analyses of samples of varying composition.

Section 14 requires analytical **quality control samples** (A.Q.C.). These are intended to demonstrate that analyses of the same substances performed by different analysts at different times and places are comparable within known statistical confidence limits. The A.Q.C. samples are in addition to the sampling quality control in Section 13. The results of the A.Q.C. samples are not to be reported to the Ministry routinely, but must be available for inspection upon request.

REPORTING

The Regulation will require the submission of **three types of information** to the Ministry. Dischargers will be required to report information on their **operations** described in Section 15 within 3 months of promulgation of the Regulation. **Analytical results,** including toxicity testing results, and **flow data** will be regularly reported on approved forms and in electronic formats to be agreed upon and suppported, where necesssary, by operational status reports.

Prior to the sampling of effluents under the Regulation, dischargers will be required to submit **information on refinery operations** (including the locations of processing areas, intakes, effluent streams, cooling water streams, storm water streams, overflows, by-passes, outfalls, sampling points and flow measurement devices), sampling methods, flow measurement methods, analytical procedures, and QA/QC procedures. Submission of a schedule of sampling dates and times and the names and addresses of all laboratories to be used will also be required, together with a reporting schedule for analyses to be performed by outside laboratories.

In addition, dischargers must submit an initial description of any **chemicals added to once-through cooling water** and submit a report on quantities used on a monthly basis. This information is essential, in order that analytical results may be properly assessed, and to facilitate Ministry audit of each discharger's monitoring program.

All analytical results, including the quality control sample results, must be submitted to the local District Office of the Ministry on prescribed forms. The forms must be submitted by the end of the month following the date of sampling.

Flow measurement information must also be reported on prescribed forms and submitted by the end of the month following the month to which the flow data pertains.

The daily maximum, minimum, and mean flow rates are to be reported for process effluent streams to permit verification of flow variability. The measured variability in flow will be compared against the flow variability criteria to assess the need for flow proportional sampling on process effluent streams.

In the past, refineries have reported net concentrations to government to account for the contamination of inlake waters. The Ministry, in this Regulation, requires the reporting of actual discharge concentrations. Inlet concentrations may be reported by the refinery to aid in the interpretation of net contributions of contaminants from that location.

The results of toxicity testing must be submitted on prescribed forms.

All of the results on the Forms **must be certified** as authentic by an official who has been authorized by the company (eg. site manager).

In addition to the Forms, the results must be submitted in an electronic format on floppy diskette. Submission of data in an electronic format will eliminate the possibility of transcription errors and will facilitate the implementation of a highly automated system of data processing. The Ministry is currently developing a program for floppy diskette which will be made available to dischargers.

APPENDIX A: COMPARISON OF CHARACTERIZATION LIST TO EMPPL

EMPPL PARAMETERS	CAS #	PETROLEUM REFINERY CHARACTERIZATION PARAMETERS	ANALYTICAL TEST GROUP #
Abietic Acid	514-10-3	NO	-
Acenaphthene	83-32-9	YES	19
Acenaphthene, 5-nitro	602-87-9	YES	19
Acenaphthylene	208-96-8	YES	19
Acridine	260-94-6	NO	-
Acrolein	107-02-8	YES	18
Acrylonitrile	107-13-1	YES	18
Aluminum	4729-90-5	YES	9
4-Aminoazobenzene	60-09-3	NO	-
Aniline	62-53-3	NO	-
Anthracene	120-12-7	YES	19
Antimony	7440-36-0	YES	10
PCB 1016	12674-11-2	YES	27
PCB 1221	11104-28-2	YES	27
PCB 1232	11141-16-5	YES	27
PCB 1242	53469-21-9	YES	27
PCB 1248	12672-29-6	YES	27
PCB 1254	11097-69-1	YES	27
PCB 1260	11096-82-5	YES	27
Arsenic	7440-38-2	YES	10
Benzaldehyde	100-52-7	NO	-
Benz(a)anthracene	56-55-3	YES	19
Benzene	71-43-2	YES	17
Benzeneacetonitrile	140-29-4	NO	-
Benzidine	92-87-5	NO	-
Benzo(b)fluoranthene	205-99-2	YES	19
Benzo(k)fluoranthene	207-08-9	YES	19
Benzo(g,h,i)perylene	191-24-2	YES	19
Benzo(a)pyrene	50-32-8	YES	19
Benzyl alcohol	100-51-6	NO	-
Beryllium	7440-41-7	YES	9
Biphenyl	92-52-4	NO	-
Bromoform	75-25-2	YES	16
Bromomethane	74-83-9	YES	16
4-Bromophenyl phenyl ether	101-55-3	YES	19
1,3-Butadiene	106-99-0	YES	18
Butanal	123-72-8	NO	-
Butylbenzylphthalate	85-68-7	YES	19
Cadmium	7440-43-9	YES	9
Camphene	79-92-5	YES	19
Carbon tetrachloride	56-23-5	YES	16
Chorinated dibenzofurans	N/A	YES	24
Chorinated dibenzo-p-dioxins	N/A	YES	24
Chlorobenzene	108-90-7	YES	16
Chlorodehydroabietic acid	57055-38-6	NO	-
Chlorodibromomethane	124-48-1	YES	16
Chloroform	67-66-3	YES	16
Chloromethane	74-87-3	YES	16
Bis(2-chloroethoxy)methane	111-91-1	YES	19

APPENDIX A: COMPARISON OF CHARACTERIZATION LIST TO EMPPL

EMPPL PARAMETERS	CAS #	PETROLEUM REFINERY CHARACTERIZATION PARAMETERS	ANALYTICAL TEST GROUP #
Bis(2-chloroethyl)ether	111-44-4	YES	19
Bis(2-chloroisopropyl)ether	108-60-1	YES	19
Bis(chloromethyl)ether	542-88-1	NO	-
4-Chloro-3-methylphenol	59-50-7	YES	20
1-Chloronaphthalene	90-13-1	YES	19
2-Chloronaphthalene	91-58-7	YES	19
2-Chlorophenol	95-57-8	YES	20
4-Chlorophenyl phenyl ether	7005-72-3	YES	19
Chromium	7440-47-3	YES	9
Chrysene	218-01-9	YES	19
Cobalt	7440-48-4	YES	9
Copper	7440-50-8	YES	9
m-Cresol	108-39-4	YES	20
o-Cresol	95-48-7	YES	20
p-Cresol	106-44-5	YES	20
Cyanide	57-12-5	YES	2
Dehydroabietic acid	1740-19-8	NO	-
Dibenz(a,h)anthracene	53-70-3	YES	19
2,6-Di-t-butyl-4-methylphenol	128-37-0	NO	-
Di-n-butyl phthalate	84-74-2	YES	19
1,2-Dichlorobenzene	95-50-1	YES	16
1,3-Dichlorobenzene	541-73-1	YES	16
1,4-Dichlorobenzene	106-46-7	YES	16
3,3'-Dichlorobenzidene	91-94-1	NO	-
1,1-Dichloroethane	75-34-3	YES	16
1,2-Dichloroethane	107-06-2	YES	16
Trans-1,2-Dichloroethylene	156-60-5	YES	16
1,1-Dichloroethylene	75-35-4	YES	16
2,4-Dichlorophenol	120-83-2	YES	20
2,6-Dichlorophenol	87-65-0	YES	20
1,2-Dichloropropane	78-87-5	YES	16
Cis-1,3-Dichloropropylene	10061-01-5	YES	16
Trans-1,3-Dichloropropylene	10061-02-6	YES	16
Bis(2-ethylhexyl)phthalate	111-81-7	YES	19
Dimethyl disulphide	624-92-0	NO	-
2,4-Dimethyl phenol	105-67-9	YES	20
4,6-Dinitro-o-cresol	534-52-1	YES	20
2,4-Dinitrophenol	51-28-5	YES	20
2,4-Dinitrotoluene	121-14-2	YES	19
2,6-Dinitrotoluene	606-20-2	YES	19
1,4-Dioxane	123-91-1	NO	-
Diphenylamine	122-39-4	YES	19
Diphenyl ether	101-84-8	YES	19
Ethylene dibromide	106-93-4	YES	16
Ethylene thiourea	1740-19-8	NO	-
Eugenol	97-53-0	NO	-
Fluoranthene	206-44-0	YES	19
Fluorene	86-73-7	YES	19
Formaldehyde	50-00-0	NO	-

APPENDIX A: COMPARISON OF CHARACTERIZATION LIST TO EMPPL

EMPPL	CAS	PETROLEUM REFINERY	ANALYTICAL
PARAMETERS	#	CHARACTERIZATION	TEST
		PARAMETERS	GROUP #
Hexachlorobenzene	118-74-1	YES	23
Hexachlorobutadiene (HCBD)	87-68-3	YES	23
Hexachlorocyclopentadiene	77-47-4	YES	23
Hexachloroethane	67-72-1	YES	23
Hydrazine	302-01-2	NO	-
Hydroxycyclohexane	108-93-0	NO	-
2-Hydroxybiphenyl	90-43-7	NO	-
4-Hydroxybiphenyl	92-69-3	NO	-
Indeno(1,2,3-cd)pyrene	193-39-5	YES	19
Indole	120-72-9	YES	19
Isopimaric	5835-26-7	NO	-
Lead	7439-92-1	YES	9
Levopimaric acid	79-54-9	NO	-
Limonene	138-86-3	NO	-
Mercapto benzothiazole	149-30-4	NO	-
Mercury	7439-97-6	YES	12
Methylene chloride	75-09-2	YES	16
Methyl ethyl ketone	78-93-3	YES	17
N-Methylformamide	123-39-7	NO	-
1-Methylnaphthalene	90-12-0	YES	19
2-Methylnaphthalene	91-57-6	YES	19
Methyl styrene	250013-15-4	NO	-
Molybdenum	7439-98-7	YES	9
Naphthalene	91-20-3	YES	19
Neoabietic acid	471-77-2	NO	-
Nickel	7440-02-0	YES	9
1-Nitronaphthalene	86-57-7	NO	-
2-Nitronaphthalene	581-89-5	NO	-
4-Nitrophenol	100-02-7	YES	20
N-Nitrosodimethylamine	62-75-9	NO	-
N-Nitrosodi-n-propylamine	621-64-7	YES	19
N-Nitrosodiphenylamine	86-30-6	YES	19
Octachlorostyrene	29082-74-4	YES	23
Oleic Acid	112-80-1	NO	-
Pentachlorobenzene	608-93-5	YES	23
Pentachlorophenol	87-86-5	YES	20
Perylene	198-55-0	YES	19
Phenanthrene	85-01-8	YES	19
Phenol	108-95-2	YES	20
Pimaric acid	127-27-5	NO	-
Pyrene	129-00-0	YES	19
Selenium	7782-49-2	YES	10
Silver	7440-22-4	YES	9
Styrene	100-42-5	YES	17
Tetrachloroacetone	31422-61-4	NO	-
1,1,3,3-Tetrachloroacetone	632-21-3	NO	-
1,2,3,4-Tetrachlorobenzene	634-66-2	YES	23
1,2,3,5-Tetrachlorobenzene	634-90-2	YES	23
1,2,4,5-Tetrachlorobenzene	95-94-3	YES	23

APPENDIX A: COMPARISON OF CHARACTERIZATION LIST TO EMPPL

EMPPL PARAMETERS	CAS #	PETROLEUM REFINERY CHARACTERIZATION PARAMETERS	ANALYTICAL TEST GROUP #
2,3,7,8-Tetrachlorodibenzo-p-dioxin	1746-01-6	YES	24
1,1,2,2-Tetrachlorethane	79-34-5	YES	16
Tetrachloroethylene	127-18-4	YES	16
Tetrachloroguaiacol	2538-17-5	NO	-
2,3,4,5-Tetrachlorophenol	4901-51-3	YES	20
2,3,4,6-Tetrachlorophenol	58-90-2	YES	20
2,3,5,6-Tetrachlorophenol	935-95-5	YES	20
Tetraethyl lead	78-00-2	Tetra-alkyl lead	13
Thallium	7440-28-0	YES	9
Thiourea	62-56-6	NO	-
Toluene	108-88-3	YES	17
Tributyl phosphate	126-73-8	NO	-
1,1,3-Trichloroacetone	921-03-9	NO	-
1,2,3-Trichlorobenzene	87-61-6	YES	23
1,2,4-Trichlorobenzene	120-82-1	YES	23
1,1,2-Trichloroethane	79-00-5	YES	16
Trichloroethylene	79-01-6	YES	16
Trichlorofluoromethane	75-69-4	YES	16
Trichloroguaiacol	61966-36-7	NO	-
2,3,4-Trichlorophenol	15950-66-0	YES	20
2,3,5-Trichlorophenol	933-78-8	YES	20
2,4,5-Trichlorophenol	95-95-4	YES	20
2,4,6-Trichlorophenol	88-06-2	YES	20
2,4,5-Trichlorotoluene	6639-30-1	YES	23
Triethyl lead	N/A	Tri-alkyl lead	13
Trimethylbenzenes	25551-13-7	NO	-
Trimethylnaphthalene	2717-42-2	NO	-
Vanadium	7440-62-2	YES	9
Vinyl chloride	75-01-4	YES	16
o-Xylene	95-47-6	YES	17
m-Xylene	108-38-3	YES	17
p-Xylene	106-42-3	YES	17
Zinc	7440-66-6	YES	9
	N/A	Ammonia plus Ammonium	4a
	N/A	Chemical oxygen demand (COD)	1
	75-27-4	Dichlorobromomethane	16
	117-81-7	Di-n-octyl phthalate	19
	N/A	Dissolved organic carbon (DOC)	5
	100-41-4	Ethylbenzene	17
	N/A	Hydrogen ion (pH)	3
	N/A	Nitrate	4b
	N/A	Nitrite	4b
		Oil and grease	25
	N/A	Phenolics (4AAP)	14
	N/A	Specific conductance	7
	N/A	Sulphide	15
	N/A	Total Kjeldahl nitrogen	4a
	N/A	Total organic carbon (TOC)	5
	N/A	Total phosphorus	6

APPENDIX A: COMPARISON OF CHARACTERIZATION LIST TO EMPPL

EMPPL PARAMETERS	CAS #	PETROLEUM REFINERY CHARACTERIZATION PARAMETERS	ANALYTICAL TEST GROUP #
	N/A	Total suspended solids (TSS)	8
	N/A	Volatile suspended solids (VSS)	8

APPENDIX B: FLOW MEASUREMENT METHODS AND DEVICES

COLUMN 1	COLUMN 2	COLUMN 3		
FLOW MEASUREMENT METHODS AND DEVICES	APPLICABLE OUTFALLS	PROOF OF CALIBRATION		
		a) PRIMARY MEASUREMENT DEVICE	b) SECONDARY MEASUREMENT DEVICE	c) ON-SITE CALIBRATION
A. PRESSURE CONDUITS (PIPE) (IN-LINE INSTALLATION)				
MAGNETIC METER - FLOW TUBE	P,C,S,L	X	X	
- INSERT TYPE	P,C,S,L	X	X	
ORIFICE PLATE	P,C,S,L	X	X	
FLOW NOZZLE	P,C,S,L	X	X	
VENTURI TUBE	P,C,S,L	X	X	
ULTRASONIC - DOPPLER	P,C,S,L	N/A	X	X
- TIME OF FLIGHT	C	X	X	
ROTOR TECHNIQUES	P,C,S,L		X	X
PROPRIETARY/CUSTOM DESIGNS	P,C,S,L	X	X	X
B. FREELY DISCHARGING PIPES (END-OF-PIPE INSTALLATION)				
NOZZLES	P,C,S,L	X	X	
ORIFICES	P,C,S,L	X	X	
TUBES	P,C,S,L	X	X	

APPENDIX B: FLOW MEASUREMENT METHODS AND DEVICES

COLUMN 1 FLOW MEASUREMENT METHODS AND DEVICES	COLUMN 2 APPLICABLE OUTFALLS	COLUMN 3 PROOF OF CALIBRATION		
		a) PRIMARY MEASUREMENT DEVICE	b) SECONDARY MEASUREMENT DEVICE	c) ON-SITE CALIBRATION
PROPRIETARY/CUSTOM DESIGNS	P,C,S,L	X	X	X
C. OPEN CHANNEL				
SHARP CRESTED WEIRS				
- RECTANGULAR	P,C,S,L		X	
- TRIANGULAR OR V-NOTCH	P,C,S,L		X	
- CIPOLLETTI	P,C,S,L		X	
- COMPOUND	S	X	X	X
- PROPRIETARY/CUSTOM DESIGNS	P,C,S,L	X	X	X
FLUMES				
- PARSHALL	P,C,S,L		X	
- VENTURI	P,C,S,L		X	
- PALMER - BOWLUS	S,C,L		X	X
- LEOPOLD - LAGCO	S,C,L		X	X
- PROPRIETARY/CUSTOM DESIGNS	P,C,S,L	X	X	X

APPENDIX B: FLOW MEASUREMENT METHODS AND DEVICES

COLUMN 1	COLUMN 2	COLUMN 3		
FLOW MEASUREMENT METHODS AND DEVICES	APPLICABLE OUTFALLS	PROOF OF CALIBRATION		
		a) PRIMARY MEASUREMENT DEVICE	b) SECONDARY MEASUREMENT DEVICE	c) ON-SITE CALIBRATION
VELOCITY - AREA METHODS	P,C,S,L	N/A	X	X
FRICTION FORMULA				
- MANNING'S EQUATION	S,C,L	N/A	X	X
OTHER HYDRAULIC STRUCTURES OR TECHNIQUES	P,C,S,L	X	X	X
D. MISCELLANEOUS METHODS				
WATER METERS (ON INCOMING LINES)	C			X
PUMPING RATES	S,C,L			X
E. NON-CONTINUOUS METHODS				
DILUTION/TRACER METHODS	*,P,C,S	N/A	X	
WET WELL DRAW DOWN	*,P,C,S,L	N/A	X	
VELOCITY - AREA	*,P,C,S	N/A	X	
VOLUME - TIME	*,P,C,S,L	N/A	X	
TRAJECTORY METHOD	S,C,L			X
CALIFORNIA PIPE METHOD	S,C,L			X

APPENDIX B: FLOW MEASUREMENT METHODS AND DEVICES

LEGEND:				
P - PROCESS EFFLUENT				
C - COOLING WATER				
S - STORM WATER				
L - LANDFARM LEACHATE				
N/A - NOT APPLICABLE				
* - NOTE 1: THESE METHODS ARE SUITABLE FOR CALIBRATION OF CONTINUOUS FLOW MEASURING METHODS. THEY CAN BE USED FOR MEASUREMENT OF FLOW RATE AT SAMPLING POINTS WITHOUT CONTINUOUS FLOW MEASUREMENT REQUIREMENT.				

SECTION III

MISA Advisory Committee Report Regarding the Effluent Monitoring Regulation for the Petroleum Refining Sector

Ontario

Ministry
of the
Environment

Ministère
de
l'Environnement

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June 17, 1987

The Honourable Jim Bradley
Minister of the Environment
135 St. Clair Avenue West
Toronto, Ontario
M4V 1P5

Dear Mr. Bradley:

I am pleased to provide you with the Report of the MISA Advisory Committee on the draft MISA Petroleum Refinery Effluent Monitoring Regulation.

The Committee members feel strongly that the regulation-specific recommendations should be incorporated into the "public draft" of the Regulation.

We assume that on the basis of your letter of January 1987, this Report will be published along with the draft regulation during the public review period.

The Committee would be pleased to discuss with you and your staff in the near future, this Report and our impressions of the process leading to the tabling of this first draft MISA regulation.

Yours sincerely,

Douglas

Douglas J. Hallett
Chairman
MISA Advisory Committee

ONTARIO MINISTRY OF THE ENVIRONMENT
MUNICIPAL-INDUSTRIAL STRATEGY FOR ABATEMENT

MISA ADVISORY COMMITTEE

REPORT regarding the

EFFLUENT MONITORING REGULATION FOR THE PETROLEUM REFINING SECTOR

June 4, 1987

Doug Hallett
Chairman

Toby Vigod
Vice-Chairman

MISA ADVISORY COMMITTEE REPORT regarding the EFFLUENT MONITORING REGULATION FOR THE PETROLEUM REFINING SECTOR

1. INTRODUCTION

The Honourable Jim Bradley, Minister of the Environment, has established as a major priority, the goal of the virtual elimination of persistent toxic contaminants (in addition to conventional pollutants) in industrial and municipal discharges into Ontario's waterways. The Municipal-Industrial Strategy for Abatement (MISA) is a program which has been developed to achieve this goal of systematically reducing the concentration of persistent toxic chemicals discharged by point sources.

MISA is to impose abatement requirements on eight major industrial sectors, and on municipal dischargers. Regulated controls under the program are to be established by effluent monitoring regulations, and subsequently by effluent limits regulations under the Environmental Protection Act.

The purpose of the effluent monitoring regulations is to develop, through a comprehensive monitoring program, a data base on effluent water quality, emphasizing toxic contaminants. The monitoring is "to reflect all conditions of operation, including normal and upset conditions, within a standardized framework of sampling and analytical quality assurance, quality control and audit". The data base will be used to evaluate current effluent water quality, and to determine the level of further treatment required to meet specific performance standards and water quality requirements. Effluent limits regulations will supercede the monitoring regulation and will include ongoing or amended monitoring requirements.

The MISA Advisory Committee (MAC) was established in late 1986 as a group of independent experts providing the MISA process and the Minister of the Environment with a "third party" opinion, emphasizing environmental protection, on the draft regulations developed (see Appendix A - Committee Terms of Reference/Membership). The committee's expertise covers a broad spectrum within the field of environmental science; biology, chemistry, toxicology, civil and chemical engineering, economics, environmental policy and law. Furthermore, when the regulation pertaining to a specific sector is under review by the MISA Advisory Committee, a representative from that sector attends as a MAC member.

The Petroleum Refinery Effluent Monitoring Regulation was developed by the Ministry of the Environment staff in consultation with the Joint Industry/Federal/Provincial Technical Committee and draft regulations of November 1986 and January, March and May 1987 were provided to MAC for review.

Past work has shown that toxic substance loadings in the Great Lakes arise from long range transport as well as from point and diffuse sources. This current MISA draft regulation aims to quantify the loading of toxic chemicals from petroleum refinery point discharges to receiving waters. The regulation should result in the gathering of data that, when supplemented with additional information will provide the basis for prescribing specific effluent limits to control the quality of refinery discharges.

The objective of MAC's review was to determine whether the draft regulation will provide enough information to quantify the loading of toxic chemicals in petroleum refinery discharges, and whether this newly developed data base will be of sufficient scope and sensitivity to permit credible assessments of toxic chemical loadings and adverse environmental impact.

2. ADVICE TO THE MINISTER

The MISA Advisory Committee regards this draft regulation as a major step forward in toxic chemical control in Ontario. However, certain improvements in the content of the regulation are necessary for inclusion prior to its promulgation to address the deficiencies discussed below. The MISA Advisory Committee has also proposed program-specific improvements to the MISA programs which support the regulatory process.

3. DEFICIENCIES IN THE DRAFT REGULATION

Deficiencies and recommendations are highlighted, since this is a critical review, intended for constructive improvement of the document. The order of discussion does not imply relative importance to the items discussed; but, rather, follows the content sequence of the draft regulation.

Explanatory Notes

The draft Petroleum Effluent Monitoring Regulation is preceded by "Explanatory Notes". These notes do not provide an adequate explanation of how and why the regulation was developed, what options were considered, how selection was accomplished, and how MISA goals will be accomplished. **MAC recommends the re-writing of the explanatory notes, or the inclusion of additional background material to address these concerns.**

A sound explanation is necessary for legislators, for industry and for the public - for all MISA participants to understand fully the new regulatory direction. The complete document would include referencing the scientific studies (eg. PACE) which were employed, as well as the draft Ontario Effluent Monitoring Priority Pollutants List (EMPPL). It is understood that the draft EMPPL will be released simultaneously as a supporting document to the regulation, along with several other studies. MAC has not reviewed the draft EMPPL document in detail, and is not in a position to endorse its content.

Specifically, in the Explanatory Notes, MAC suggests the rewording of paragraph 6 on page 1, to become "Secondary biological treatment, and oil removal facilities have been installed, bringing the refineries to a generally high level of effluent water treatment". Also in the continuation onto page 2, the sentence "There is no implication that the refineries cause major environmental problems" should be removed as being prejudicial to the results of the monitoring program.

Characterization

MAC is concerned by the limitations of the open characterization proposed in the audit program to be carried out by the Ministry. The assigned detection limit of 50 ppb could preclude the identification of significant loadings of persistent toxic chemicals. **MAC recommends that these limits be lowered to a compound-specific level, and data should be reported for each compound down to the 1 to 20 ppb range. Method Detection Limits (MDL's) and variability of test results should be reported.**

MAC also recommends that alkylated polyaromatic hydrocarbons (PAH), mercaptans, thiophenes, ketones and alkylated phenolics, which were identified in the PACE studies, be assessed for inclusion in the EMPPL and, subject to meeting appropriate criteria, be included in the characterization list.

Routine Monitoring

It is MAC's belief that all chemical monitoring under the regulations should be directed to a specific understanding of the inter-relationships between detection levels, variability of test results, effluent water flow and the calculation of loadings and chronic toxic effects. It is therefore important to develop the analytical methods which will permit the detection and quantification of particular chemicals, and which will permit the calculation of loadings that produce serious environmental impacts. For the persistent toxic chemicals, methods to identify concentrations in the 1 ppb range may be necessary for the calculation of loadings which are significant to receiving ecosystems.

The MISA Advisory Committee is concerned with the quarterly monitoring program, as this is the component which provides the basis for the calculation of loadings. Loading calculations are presently the only measure indicating exposure to persistent toxic chemicals. Concerns relate to sampling and analytical methodologies, specifically levels of detection. MAC contends that at effluent water flow rates from some refineries, the 10 ppb method detection level will fail to reveal significant loadings of persistent toxic chemicals.

MAC recommends the development of a data base for persistent toxic compounds which will enable the measurement of loadings of toxics down to the 10 to 100 kg/year level. The calculation of such loadings will only be possible if detection levels by validated methods are available in the near term down to 1 ppb or the MDL level. Therefore, for this regulation MAC recommends **that data for all persistent toxic compounds be reported down to the 1 ppb level or the Method Detection Limit achievable for each specific compound.** Also each laboratory should report the MDL and the variability for each parameter. The Ministry should determine MDL's using spiked refinery effluents. Inter-laboratory variability also needs to be determined. All this data is required to ensure proper interpretation of chemical loading data at the end of the MISA phase 1 monitoring program.

In addition, the Ministry of the Environment should undertake a research program to validate more sensitive analytical methods for specific groups of priority toxic compounds, over the next twelve months.

MAC is concerned that certain groups of persistent organic compounds, detected and reported in PACE studies (alkylated polyaromatic hydrocarbons including methylated groups, mercaptans, thiophenes, ketones and alkylated phenolics) are not adequately represented in the monitoring schedules or the EMPPL. Therefore, **MAC recommends that these compounds should be assessed by June 1988 within the EMPPL process,** and priority compounds with confirmed or validated protocols should, within one year of the filing of the regulation, be reported quarterly at a detection limit in the range of 1 part per billion.

Listing/Delisting Mechanism

The MISA Advisory Committee recognises the paramount importance of developing a "Listing/Delisting Mechanism" for the entire MISA process. It is essential that after 12 months of intensive monitoring, the data be assessed in order to:

1. eliminate, add or reschedule certain parameters in the interest of scientific economy and to ensure the availability of sufficient data at needed levels of detection and frequency of sampling for the next phase of the MISA program, ie. development of an effluent limits regulation.
2. determine the need for the development or validation of analytical methods;
3. identify any toxic chemicals that may require more intensive monitoring scrutiny; and
4. estimate chemical loadings to the environment and the confidence limits associated with these estimates.

For this reason, **MAC recommends that a Listing/Delisting Development Task Group** consisting of technical representatives from the MOE, two or more industry sectors and the MAC **be struck immediately to develop a Listing/Delisting Mechanism within the next six months.** Each MISA sector will ultimately require a standing listing/delisting committee to revise through negotiations, that specific sector's monitoring/abatement program.

Acute Toxicity Testing

Toxicity tests, both acute and chronic, represent a second means of detecting the presence and effects of deleterious compounds. Past experience (EPA documentation) has shown the merit of this approach and there is an increasing movement towards comprehensive toxicity assessment programs (eg. Michigan).

MAC recommends that the rainbow trout testing continue, with the immediate addition of Daphnia spp, testing, which is used in industrial and municipal effluent testing on a site-specific basis throughout the United States and is available for use in Canada to pre-test pesticides. **Daphnia spp,** is recommended as a minimum to allow testing of effluents on a second native biological species which is more sensitive than rainbow trout to many pollutants.

In addition, **MAC recommends that protocols for flow-through testing using various organisms such as rainbow trout and Daphnia spp, be validated within a research program and implemented as soon as possible within the regulation process.** The testing requirements should be applied equally to all sectors. Flow-through testing is recommended in addition to static testing because it provides for the integration of exposure to chemicals in effluents over long time periods, which is the concern of the MISA initiative. As well, static tests do not provide a basis for the assessment of volatile compounds.

Chronic Toxicity Testing

Existing legislation addresses the control of conventional pollutants, and acute toxicity. The MISA regulations attempt to go beyond this to assess loadings and chronic toxicity. Chronic toxicity studies aim to assess the biological effects of exposure to compounds at low concentrations over extended periods of time. Lakewide ecological effects can be caused by the aggregated loading of pollutants which in effluents are perceived to appear in minute quantities, particularly in comparison with the higher concentrations which may cause acute effects.

The only method now available for the assessment of chronic toxicity is mathematical extrapolation from the results of acute toxicity studies. Recognizing both the importance of chronic toxicity testing, and the lack of validated chronic test methods, **MAC recommends that the Ministry research and develop valid chronic tests over the next two-year period. Validated tests should then be incorporated in subsequent monitoring and limits regulations.**

Spills

It is understood that spills may contribute significant chemical loadings relative to continuous discharges. Current regulations require the reporting of spills to the Ministry. **These reports should be provided routinely by the Ministry and in satisfactory detail within the MISA program to provide useful information for the calculation of chemical loadings.**

4. REGULATION-SPECIFIC RECOMMENDATIONS

4.1 Rationale

That the Explanatory Notes should be re-written, or a supplementary document should be prepared to become a more comprehensive "rationale" for the regulation and that the regulatory framework should be described, especially in the context of Ontario and interjurisdictional requirements under the Great Lakes Water Quality Agreement, and in regard to the commitment to the elimination of persistent toxic discharges.

4.2 Routine Monitoring

That data for all persistent toxic compounds be reported down to the 1 ppb level or the Method Detection Limit achievable for each specific compound. Also each laboratory should report the MDL and variability for each parameter. Interlaboratory variability should then be determined.

4.3 Acute Toxicity Testing

That the acute, rainbow trout toxicity testing program be maintained, with the addition to the monitoring regulation requirements of **Daphnia spp** testing, using validated protocols, for interpretation of results and determinations of test variability to be developed and/or confirmed by the Ministry over the next six months, prior to enforcement under the regulation, and equally and sequentially applied to all sector regulations.

4.4 Schedules

That the four schedules accompanying the draft regulation should appear in a form consistent with the draft Ontario Effluent Monitoring Priority Pollutants List (EMPPL), and that full references and legends be provided for all columns and headings. The derivation of the regulation schedules from the EMPPL should be fully explained.

5. PROGRAM-SPECIFIC RECOMMENDATIONS

5.1 Chemical Monitoring

That the Ministry of the Environment should undertake a research program to validate more sensitive analytical methods for specific groups of priority toxic compounds, over a one year period.

That the groups of persistent organic compounds, detected and reported in PACE studies (alkylated polyaromatic hydrocarbons (including methylated groups), mercaptans, thiophenes, ketones and alkylated phenolics) be assessed in the EMPPL process within one year, and priority compounds with confirmed or validated protocols should, within one year of the filing of the regulation, be reported quarterly at a detection limit in a range close to 1 part per billion, and be subject to listing/delisting and inclusion in the characterization list.

5.2 Characterization

That for the open characterization program, the specified limit of detection of 50 ppb be lowered to a compound-specific level, and data should be reported for each compound down to the '1 to 20 ppb' range, along with the MDL and test results variability data.

5.3 Listing/Delisting Mechanism

That a Listing/Delisting Development Task Group consisting of technical representatives from the MOE, two or more industry sectors and the MAC be struck immediately to develop a Listing/Delisting Mechanism within the next six months.

5.4 Acute Toxicity Testing

That the Ministry expand acute toxicity testing programs to include validated tests for a broader range of biota beyond **Daphnia spp**. Validated tests should be developed for possible inclusion in subsequent monitoring and effluent limits regulations, to be applied to all sectors equally and sequentially.

That protocols for flow-through testing using various organisms such as rainbow trout and **Daphnia spp** should be validated under a research program, with regulatory requirements to be applied equally and sequentially in subsequent regulations.

5.5 Chronic Toxicity Testing

Recognizing the importance of chronic toxicity testing, and the lack of validated tests, **that the Ministry research and develop valid chronic tests over the next two-year period.** Validated tests should then be incorporated in subsequent monitoring and limits regulations or control programs. Progress on the development of validated programs should be reviewed and reported on an annual basis.

5.6 Spills

That Ministry procedures under the MISA program be developed for the internal transfer and assessment of spill information currently being obtained by the MOE under existing legislation.

Submitted, June 4, 1987

MISA ADVISORY COMMITTEE

Douglas

Doug Hallett, Chairman

Toby Vigod

Toby Vigod, Vice Chairman

Monica Campbell

Monica Campbell, Member

Harvey H. Clare

Harvey Clare, Member

Paul Hebert

Paul Hebert, Member

Don MacKay

Don MacKay, Member

J.W. MacLaren

James MacLaren, Member

Kai

Kai Millyard, Member

R.A. Shaver

Ray Shaver, Member representing the Petroleum Sector

APPENDIX 1A

MISA ADVISORY COMMITTEE TERMS OF REFERENCE

The Committee is established by Order in Council 2766/86 pursuant to clause 3 (i) of the Environmental Protection Act, R.S.O. 1980, c. 141. and is empowered to provide advice to the Minister of the Environment in accordance with the White Paper "Municipal-Industrial Strategy for Abatement (MISA)" released in June 1986 and more particularly:

(a) to review draft regulations relating to monitoring and effluent limits prepared by nine sectoral technical committees;

(b) to liaise and work with the technical committees;

(c) to provide advice and recommendations to the Minister on the contents of the regulations; and

(d) to provide advice with respect to such other related matters as the Minister may prescribe.

APPENDIX 1B

MISA ADVISORY COMMITTEE PERMANENT MEMBERSHIP

Douglas J. Hallett (Chairman)

Dr. Hallett is an accomplished environmental biologist, biochemist and analytical chemist. He is president of Eco Logic, a firm which is developing and patenting a hazardous waste destruction device. In addition, he is retained as an expert on Great Lakes water quality issues, human exposure to PCB's and environmental risk assessment matters. Previously, he was Senior Scientific Advisor with Environment Canada (Ontario Region) and is a recognized expert on the technical and regulatory aspects of pollution control in Canada.

Toby E. Vigod (Vice-Chairman)

Ms. Vigod is Counsel with the Canadian Environmental Law Association. She represents clients on a variety of matters pertaining to environmental law. Her main areas of legal expertise are in the fields of toxic chemical and pesticide regulation and legislation which controls hazardous waste and Great Lakes pollution.

Monica E. Campbell

Dr. Campbell is a graduate of the Toxicology Program at the University of Toronto. Her doctoral research entailed the development of biological markers of environmental contaminant exposure. Previously, she was a researcher with the Pollution Probe Foundation, where she specialized in drinking water quality and industrial waste reduction and recycling, on which she co-authored several publications.

Harvey H. Clare

Mr. Clare is a retired former executive with Imperial Oil. From 1969 to 1982 he was the Environmental Protection Coordinator for Imperial Oil; prior to that he held, among other positions, Manager for Planning & Investment Logistics, and Manager for the Refining Coordination Division. Mr. Clare is a past president and founder of the Petroleum Association for Conservation of the Canadian Environment (PACE). He is also a former treasurer of the Conservation Council of Ontario.

Paul N. Hebert

Dr. Hebert is a Professor of Biology with the Great Lakes Institute, University of Windsor. He specializes in population biology of aquatic organisms, particularly in response of toxic contamination. His latest research efforts have concentrated on contamination of the Huron-Erie Corridor and other Great Lakes locations and encompass a range of technical and policy aspects.

James W. MacLaren

Mr. MacLaren, formerly the President with the consulting firm James. F. MacLaren and Associates, now runs his own small private consulting firm in Toronto, specializing in environmental engineering and policy management advisory services. Mr. MacLaren is a Fellow of the Engineering Institute of Canada and of the Canadian Society for Civil Engineers, a past president of the Association of Consulting Engineers of Canada, and recently, one of the three members in the "Inquiry for the Canadian Government on Federal Water Policy".

Donald MacKay

Dr. MacKay is a Professor at the University of Toronto, cross-appointed to the departments of Chemical Engineering and Applied Chemistry and the Institute for Environmental Studies. His research encompasses a range of environmental areas, namely the impact of oil spills, the dynamics of organic contaminants - particularly in the Great Lakes ecosystem, and partitioning and solubility studies. His modelling of environmental systems is of particular note with respect to aquatic-based pollution control methods.

Kai Millyard

Mr. Millyard is a researcher with the Pollution Probe Foundation. His duties include research, policy formulation, public education and advocacy on a wide range of environmental issues. His expertise lies in the field of drinking water quality, Great Lakes water pollution, hazardous waste management and acid rain. Through membership in various local, provincial, national and international boards and committees, he is conversant with a variety of pollution control efforts.

APPENDIX 1C

MISA ADVISORY COMMITTEE ROTATING SECTOR MEMBERSHIP

A member is appointed to the MISA Advisory Committee by the industrial and municipal sectors, when regulations specific to the individual sector are deliberated. The representative of the Petroleum Sector on the MISA Advisory Committee, appointed by the Ontario Petroleum Association is:

Ray Shaver

Since 1983, Ray has been Manager, Government Relations, Texaco Canada Inc. Graduating from McGill University as a chemist, Ray has worked with Texaco for 32 years and has coordinated environmental protection activities for Texaco's refinery department. In 1970, Ray assumed the position of corporate environmental affairs coordinator and in 1980 became manager for Alternate Energy and Petrochemical Development.

Mr. Shaver has held a number of senior positions with petroleum industry associations. Notably, Ray was president of the Ontario Petroleum Association from October 1985 to February 1987, and continues as a Director. Ray has served on the Board of Directors and as President of PACE (Petroleum Association for the Conservation of the Canadian Environment). In the 1960's Ray was one of the founding members and served as chairman of the Air and Water Quality Control Committee of the Canadian Manufacturer's Association. Ray is currently on the Board of Directors of the Institute for Political Involvement.

SECTION IV

Responses to the MISA Advisory Committee Recommendations on the Draft Regulation

RESPONSES TO THE MISA ADVISORY COMMITTEE RECOMMENDATIONS ON THE DRAFT REGULATION

Throughout the Regulation Development Process, the MISA Advisory Committee (MAC) has reviewed selected drafts of the Regulation and provided comments to the Joint Industry/ Government Technical Committee for the Petroleum Refining Sector (JTC). Many of these comments have been accepted and incorporated into successive versions of the Draft Regulation package. The MAC, after reviewing the penultimate draft, had submitted its final report which is available for public review.

A synopsis of major recommendations from MAC and the corresponding Joint Technical Committee responses is provided herein. Further details are contained in the MAC's final report and in the "Explanatory Notes" of the regulation package.

A. REGULATION-SPECIFIC RECOMMENDATIONS

A.1 Rationale

MAC's Recommendation

That the "Explanatory Notes" should be re-written, or a supplementary document should be prepared to become a more comprehensive "rationale" for the regulation and that the regulatory framework should be described, especially in the context of Ontario and interjurisdictional requirements under the Great Lakes Water Quality Agreement, and in regard to the commitment to the elimination of persistent toxic discharges.

MOE/JTC Response

"Explanatory Notes" are intended for elaborating technical details in sampling and analytical procedures, and data reporting requirements in the regulation, and should stay in its present form. However, during the successive revisions of the "Explanatory Notes", substantial additions have been made relating to rationale.

The very sizeable amount of information and data collected, compiled, analyzed, and reported upon (in the form of Committee minutes, working documents, discussion papers, reports and reference documents) will be made available for public review. These documents contain the "rationale" upon which the regulation requirements have been derived.

To further address MAC's concern, however, the Ministry has provided a layman's overview to explain regulation requirements to the public, including a prescriptive to put the regulatory framework in a context of Ontario's commitment under the Great Lakes Water Quality Agreement.

A.2 Routine Monitoring

MAC's Recommendation

That data for all persistent toxic compounds be reported down to the 1 ppb level or the Method Detection Limit (MDL) achievable for each specific compound. Also each laboratory should report the MDL and variability for each parameter. Interlaboratory variability should then be determined.

MOE/JTC Response

Agree with MAC's recommendation, and will work with private laboratories on this task. Compound specific MDLs will be determined for the Volatiles and Extractables, Base neutral and Acid (Phenolics) using industry and Ministry generated data through the procedure outlined in the USEPA Federal Register, CFR 40, October 26, 1984, Appendix B. These MDLs will replace the interim values, listed in Schedule 3, within 5 months of the date of promulgation of the Regulation (i.e., one month before the Regulation takes effect). MDLs currently specified in the regulation for the remaining organic chemicals range between 0.3 nanograms per litre (ppt) and 100 nanograms per litre (ppt).

A.3 Acute Toxicity Testing

MAC'S Recommendation`

That the acute, static, rainbow trout toxicity testing program be maintained, with the immediate addition to the monitoring regulation requirements of Daphnia spp. testing, using validated protocols and methodology for interpretation of results (addressing test variability) to be developed and/or confirmed by the Ministry over the next six months, prior to enforcement under the regulation, and equally and sequentially applied to all sector regulations.

MOE/JTC Response

Agree with MAC's recommendation in principle. Legal counsel advises that, in any case, an amending regulation is required to bring new test protocols/methology into effect. The Ministry will work with industry and the Federal Government to develop the test protocol for Daphnia spp. within 3-4 months. Validation of a protocol would normally include peer review and "round-robin" testing involving labs and agencies. The completion of such a test cycle may require an additional 6-8 months. Methodology for interpretation of test results will also be developed during the same period.

It is, therefore, logical to forecast that the Daphnia testing requirement and the validated protocols will be added to the current regulation (through amendment) over the next 9-12 months.

A.4 Schedules

MAC's Recommendation

That the four schedules accompanying the draft regulation should appear in a form consistent with the draft Ontario Effluent Monitoring Priority Pollutants List (EMPPL), and that full references and legends are provided for all columns and headings. The derivation of the regulation schedules from the EMPPL should be fully explained.

MOE/JTC Response

The four schedules accompanying the draft Regulation have now been consolidated into three. These schedules should stay in their present form because they are clear, precise and in legal format. In addition, the parameters in the schedules are categorized into standard test groups which are convenient for sampling and lab analysis.

To address MAC's concerns, a table will be included in the "Explanatory Notes" to cross-reference the chemicals in the schedule with the EMPPL. The "rationale" for the derivation of regulation schedules from EMPPL will be briefly explained.

B. PROGRAM-SPECIFIC RECOMMENDATIONS

B.1 Chemical Monitoring

MAC's Recommendation

That the Ministry of the Environment should undertake a research program to validate more sensitive analytical methods for specific groups of priority toxic compounds, over a one year period.

That the groups of persistent organic compounds, detected and reported in PACE studies alkylated polyaromatic hydrocarbons (including methylated groups), mercaptans, thiophenes, ketones and alkylated phenolics be assessed in the EMPPL process within one year, and priority compounds with confirmed or validated protocols should, within one year of the filing of the regulation, be reported quarterly at a detection limit in a range close to 1 part per billion, and be subject to listing/delisting and inclusion in the characterization list.

MOE/JTC Response

Agree with MAC's recommendation. The Ministry will work with industries to confirm the presence of these and any additional compounds, assess them in the EMPPL process and develop protocols on a priority basis for their analysis with MDLs as close to 1 ppb as possible. The additional EMPPL chemicals, with proven routine analytical protocols developed, will then be added to the regulation at the same time as the listing/delisting mechanism.

B.2 Effluent Characterization

MAC'S Recommendation

That for the open characterization program, the specified limit of detection of 50 ppb be lowered to a compound-specific level, and data should be reported for each compound down to the "1 to 20 ppb" range, along with Method Detection Limit (MDL) and test results variability data.

MOE Response

Agree with MAC's recommendation. The Ministry, in its open-end effluent characterization program, will identify and quantify all compounds present in the effluent at state-of-the-art detectable concentrations as compared to an internal standard (i.e., as close to 1 ppb as possible, depending upon the specific analyte and the sample matrix).

B.3 Listing/Delisting Mechanism

MAC's Recommendation

MAC recommends that a Listing/Delisting Development Task Group consisting of technical representatives from the MOE, two or more industry sectors and the MAC be struck immediately to develop a Listing/Delisting Mechanism within the next six months.

MOE/JTC Response

Agree with MAC's recommendation on the immediate formation of a Listing/Delisting Development Task Group. However, Task Groups should be formed on a single sector basis with MAC's participation. The first Task Group (Petroleum Refining Sector) is scheduled to start working in July of this year.

Based on past experience, formation and operation of a committee involving more than one sector will greatly retard the development process due to the technical differences between the individual sectors, and the different regulation timetables.

The Listing/Delisting Mechanism is being developed by the Petroleum Refining Sector Technical Committee. The Mechanism will then establish common principles to be applied sector to sector in order to develop a generic listing/delisting mechanism.

The Mechanism will be developed as soon as possible but no later than 1 year after the promulgation of this regulation. It can be introduced either through amendment to the current Monitoring Regulation or through specification in the subsequent Effluent Limits Regulation.

The Mechanism will take effect only after the monitoring requirements under the Regulation have been completed (i.e. after an equivalent of one year of data have been gathered).

B.4 Acute Toxicity Testing

MAC's Recommendation

That the Ministry expand acute toxicity testing programs to include validated tests for a broader range of biota beyond Daphnia spp. Validated tests should be developed for possible inclusion in subsequent monitoring and effluent limits regulations, to be applied to all sectors equally and sequentially.

That protocols for flow-through testing using various organisms such as rainbow trout and Daphnia spp. should be validated under a research program, with regulatory requirements to be applied equally and sequentially in subsequent regulations.

MOE Response

Agree with MAC's recommendation in principle. The Ministry will accelerate development of test protocols for species other than trout and Daphnia spp., as well as for flow-through testing.

Sound, validated and cost-effective test protocols will be included into subsequent regulations.

B.5 Chronic Toxicity Testing

MAC's Recommendation

Recognizing the importance of chronic toxicity testing, and the lack of validated tests, MAC recommends that the Ministry research the development of valid chronic tests over the next two-year period. Validated tests could then be incorporated in subsequent monitoring and limits regulations or control programs. Progress on the development of validated programs should be reviewed and reported on an annual basis.

MOE Response

Agree with MAC's recommendation and will carry out the research and development program in co-operation with Environment Canada. Evaluation of chronic testing is already underway in the Ministry's laboratories with more sensitive species, such as water fleas and with more than one life stage of test fish.

Appropriate chronic toxicity testing would be useful to detect and quantify subtle long-term problems caused by effluent discharges. However, cost-effective protocols may take a long time to be developed and validated. Until practical protocols and interpretation techniques are developed, chronic toxicity testing on site-specific basis would best be used for the purpose of water quality impact evaluations.

B.6 Spills

MAC's Recommendation

That Ministry procedures under the MISA program be developed for the internal transfer and assessment of spill information currently being obtained by the MOE under existing legislation.

MOE Response

Agree with MAC's recommendation. The Ministry will ensure that the database for the Petroleum Refineries will be kept up-to-date with reports provided by the Spill Action Centre. If this existing mechanism proves inadequate, the Ministry will review the need and the mechanisms for a more explicit reporting of spills, including all relevant information, in order to enable the assessment of contaminant loadings (and their environmental effects) from spills.

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The effluent monitoring
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